

# **Fundamental Mechanisms, Predictive Modeling, and Novel Aerospace Applications of Plasma Assisted Combustion**

**Yiguang Ju**

**AFOSR MURI Review Meeting**

**Ohio State University  
Nov 9-10, 2011**

**Princeton Team members:**

**Wenting Sun, Joe Lefkowitz, Mruthunjaya Uddi, Sang Hee Won**

**Collaborators**

**AFRL: Campbell Carter, Timothy Ombrello**

**International: Fei Qi, Huijun Guo (USTC)**

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE <b>NOV 2011</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2011 to 00-00-2011</b>	
4. TITLE AND SUBTITLE <b>Fundamental Mechanisms, Predictive Modeling, and Novel Aerospace Applications of Plasma Assisted Combustion</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Princeton University, Princeton, NJ, 08544</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>U.S. Government or Federal Rights License</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>44</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

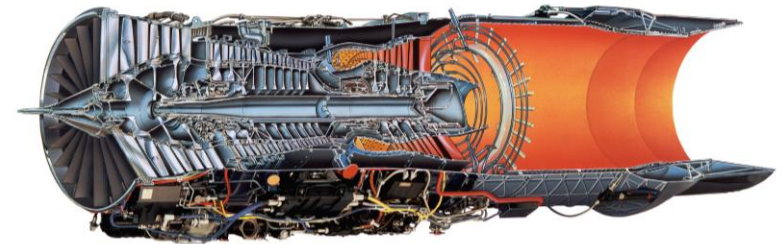


# Motivation

## Hypersonic propulsion system



## F135 engine: (F35, 2011)



## Ignition instability

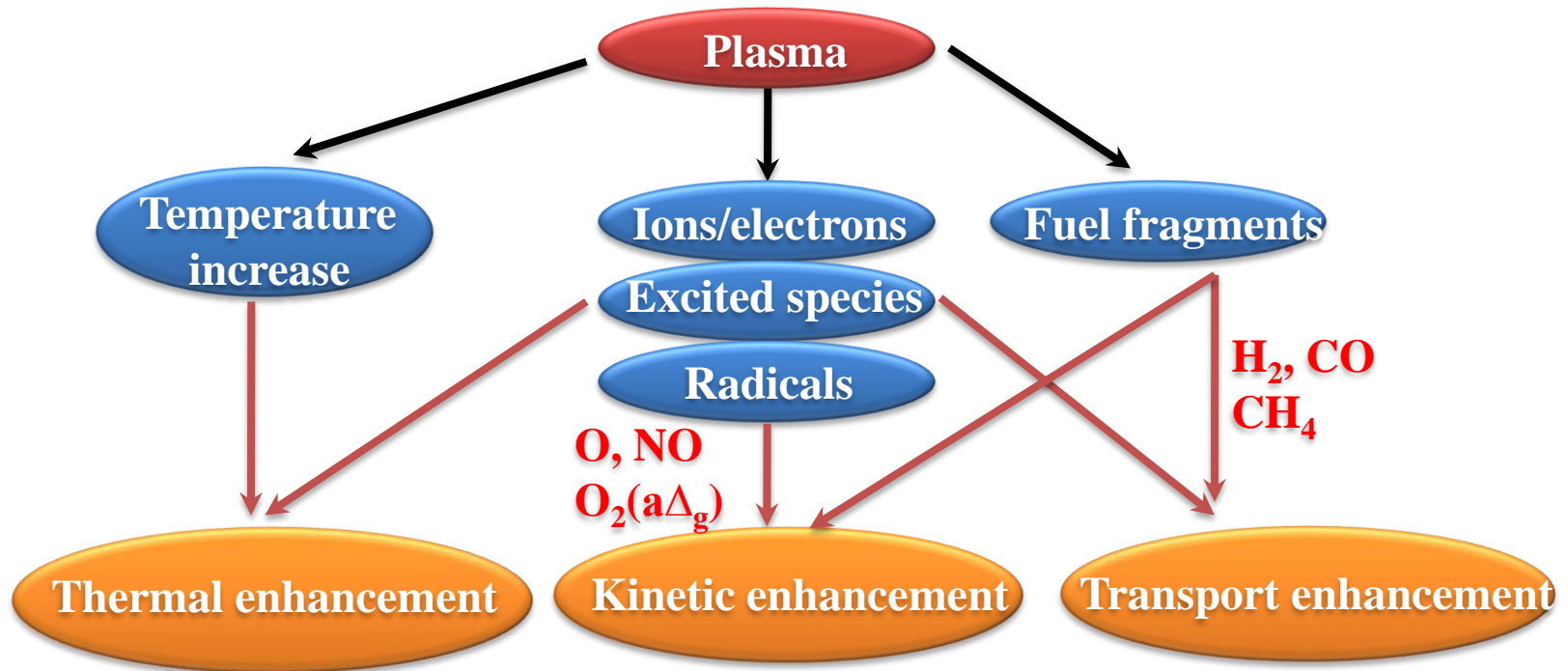
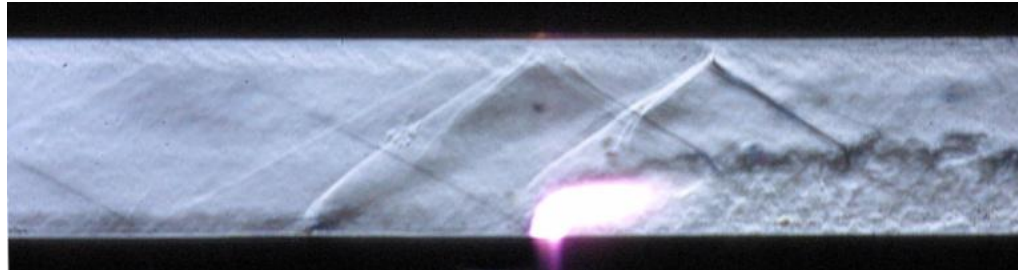
$$Da = \frac{\text{Ignition time } (\sim 10\text{ms})}{\text{Flow residence time } (\sim 1\text{ms})} \gg 1$$

## Challenges:

- Ignition time, Ignition energy
- Flame stabilization
- Combustion completion



# Plasma assisted combustion



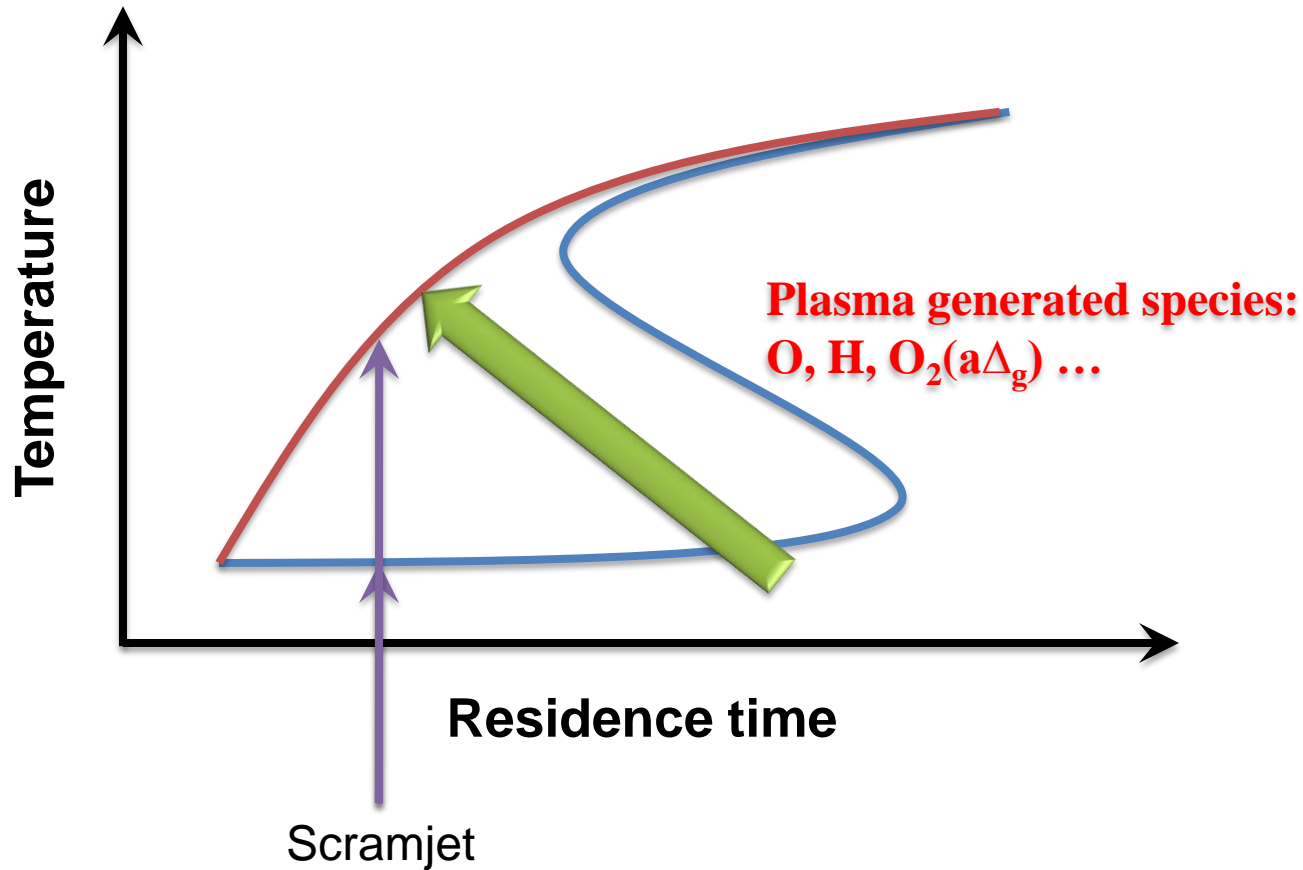
Understanding: Good

poor

marginal



## Change of ignition and extinction diagram: the S-curve transition





# Research goals

**Understand the fundamental enhancement mechanism of plasma-flame chemistry**

**Develop new experimental tools to validate plasma flame kinetic mechanism**

**Develop numerical methods to achieve efficient modeling of detailed plasma flame chemistry**



# Outline

## 1. Background

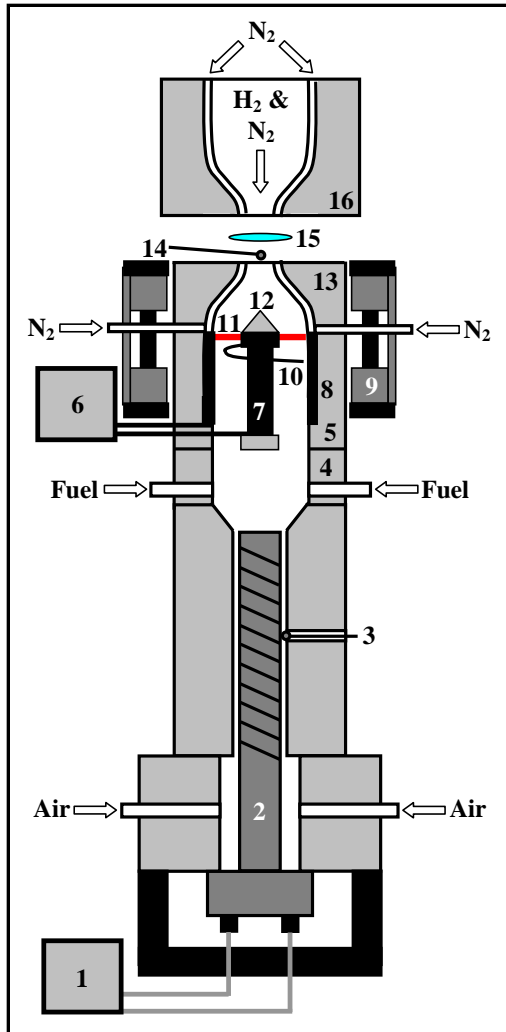
## 2. Experimental investigations

- Effects of plasma assisted fuel oxidation on flame extinction
- Effects of *in situ* plasma discharge on ignition enhancement
- Molecular beam mass spectrometry study of low temperature chemistry

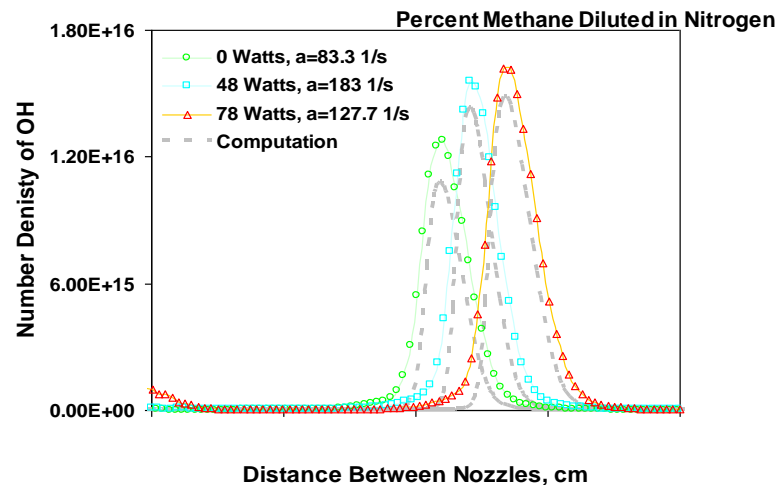
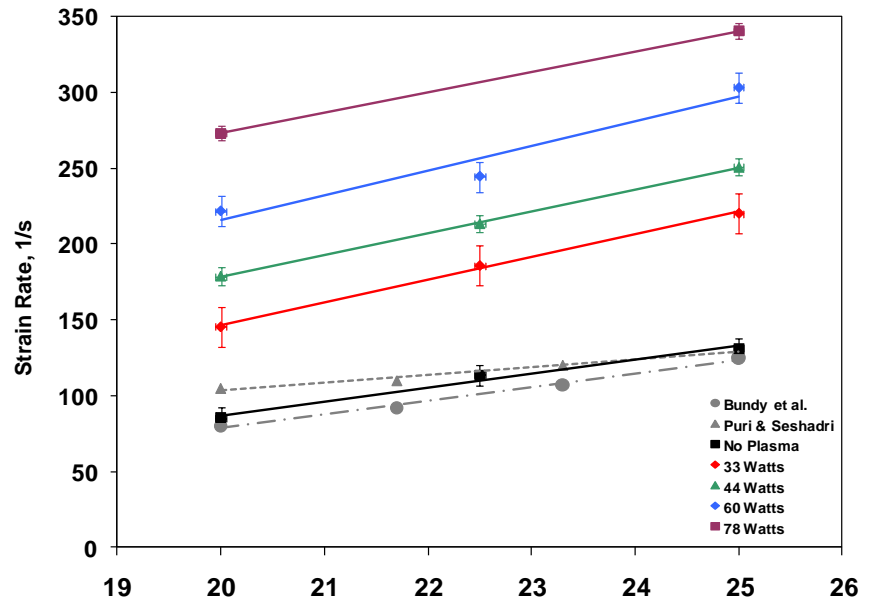
## 3. Conclusion and future work



# Background and previous study: flame extinction



1. Silicon Controlled Rectifier, 2. Silicon carbide heater, 3. R-type thermocouple, 4. Fuel injection spacer 5. MGA plasma power supply, 5. MGA device, 6. MGA power supply, 7. Cathode, 8. Anode, 9. Magnets, 10. Gliding arc initiation wire, 11. MGA, 12. Insulator, 13. Nozzle with  $N_2$  co-flow, 14. K-type thermocouple & FT-IR probe, 15. Diffusion flame, 16. Water-cooled nozzle with  $N_2$  co-flow.



**Only thermal effect!**

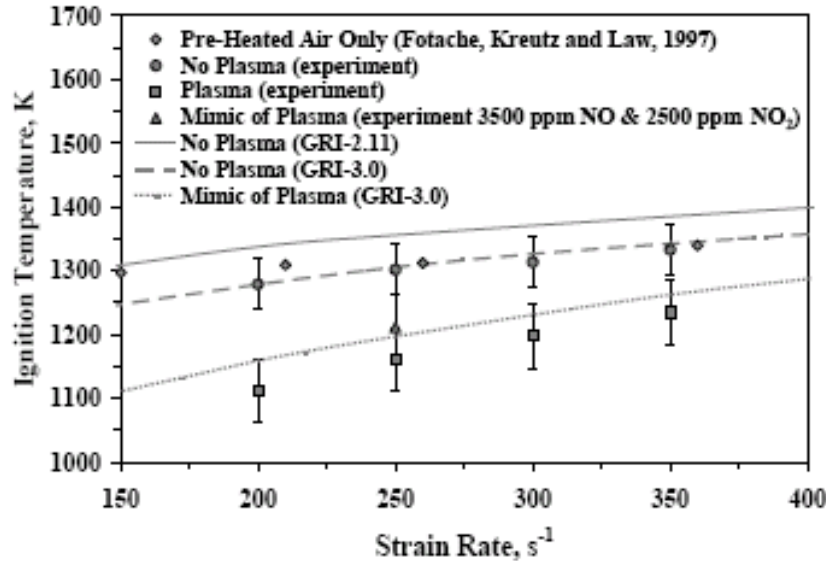
Ombrello, et al, AIAA J, 2006



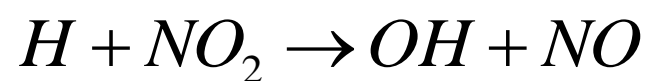
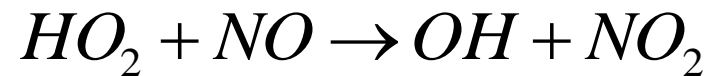
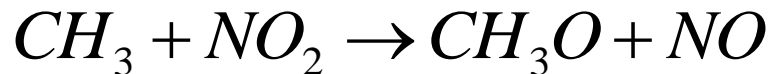
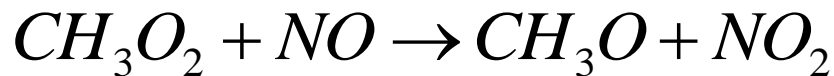
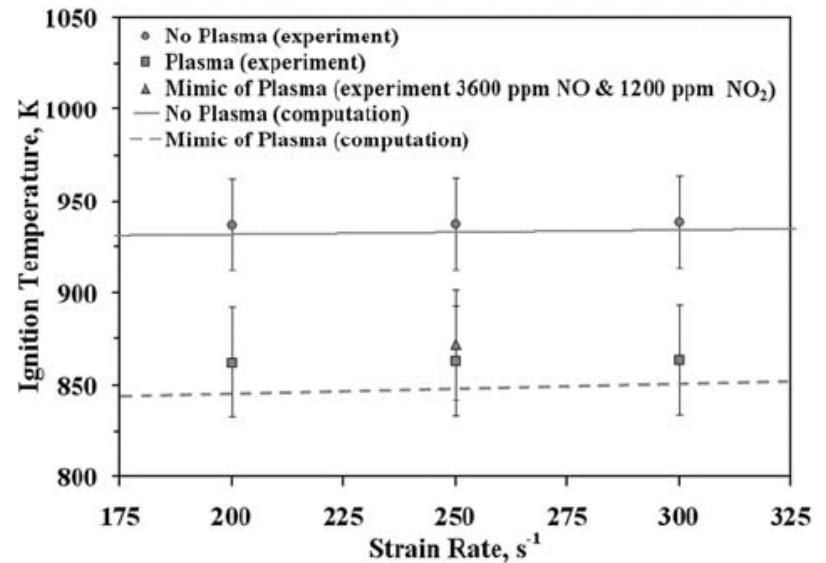


# Previous work - Ignition study

CH<sub>4</sub>/air counterflow diffusion flame



H<sub>2</sub>/air counterflow diffusion flame



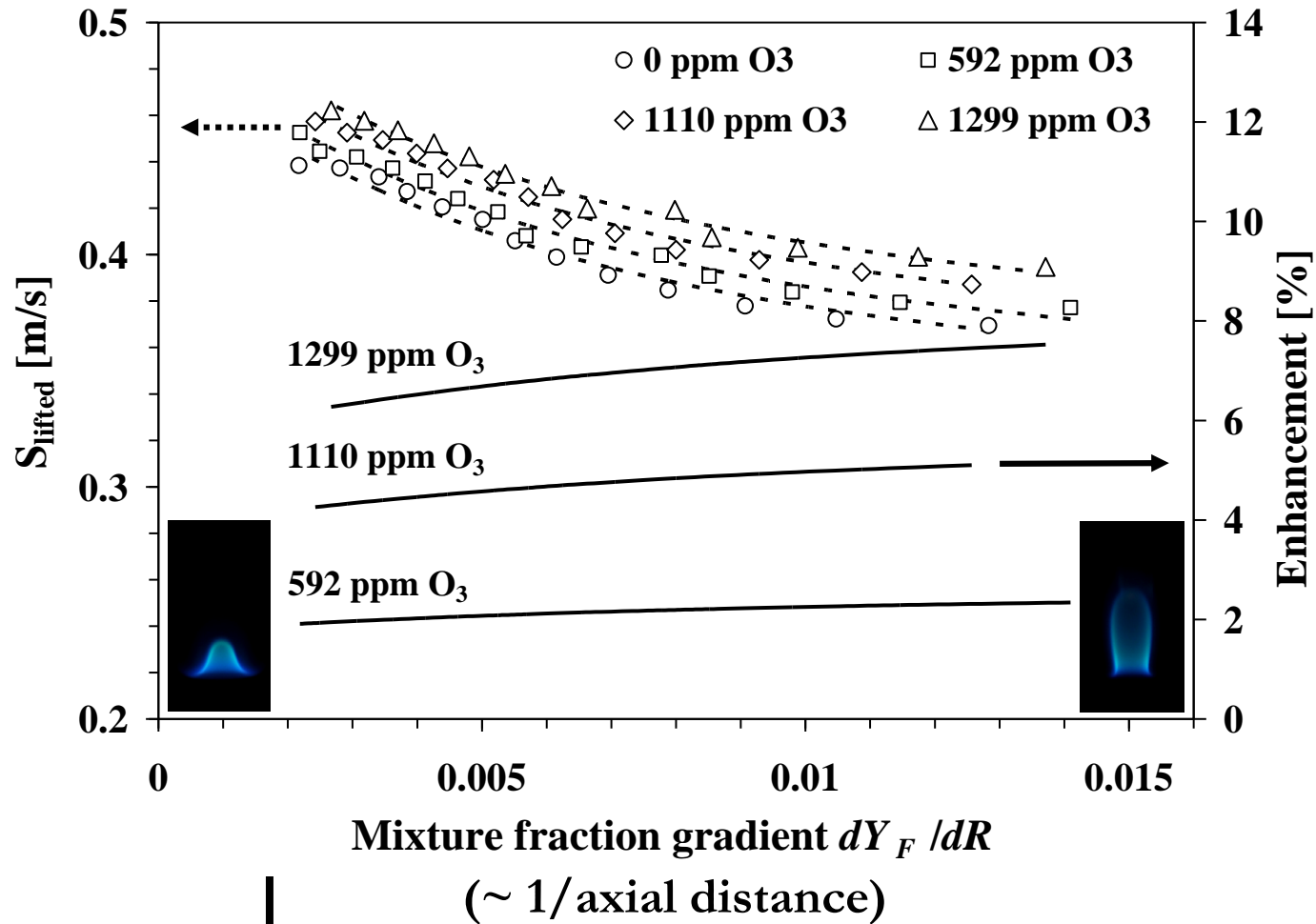
**NO<sub>x</sub> catalytic effect**

**1. non *in situ* discharge**

**2. Short life times of radicals and excites species**



# Previous researches – O<sub>3</sub>



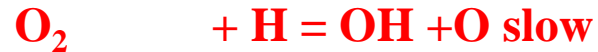
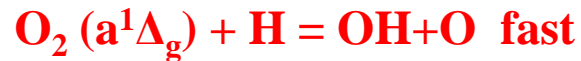
$$S_L \approx S_{\text{lifted}} \sqrt{\frac{\rho_b}{\rho_u}}$$

Flame speed extraction

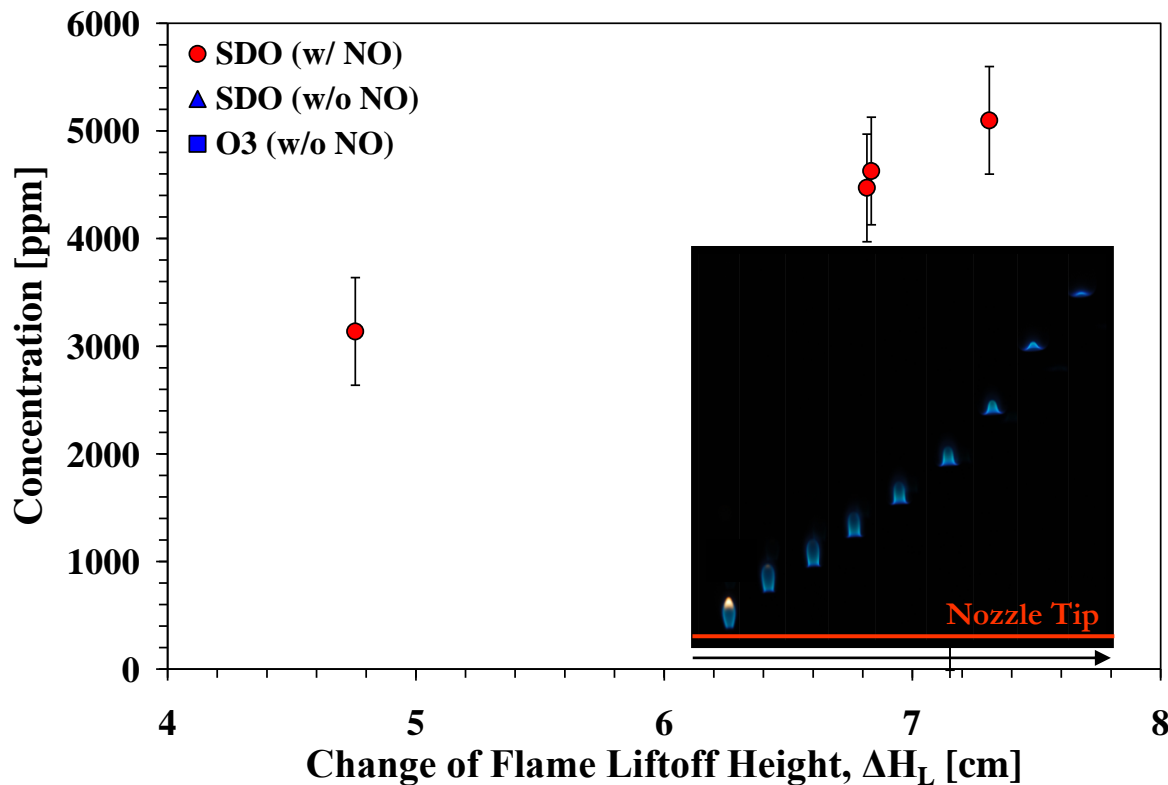


# Previous researches – $O_2(a^1\Delta_g)$

$[O_2(a^1\Delta_g)]$ , ppm	$\Delta H_L$ , mm
3137	4.76
4470	6.82
4627	6.83
5098	7.31



→  $\approx 5000$  ppm  $O_2(a^1\Delta_g)$  → 2-3 % Lifted Flame Speed Enhancement

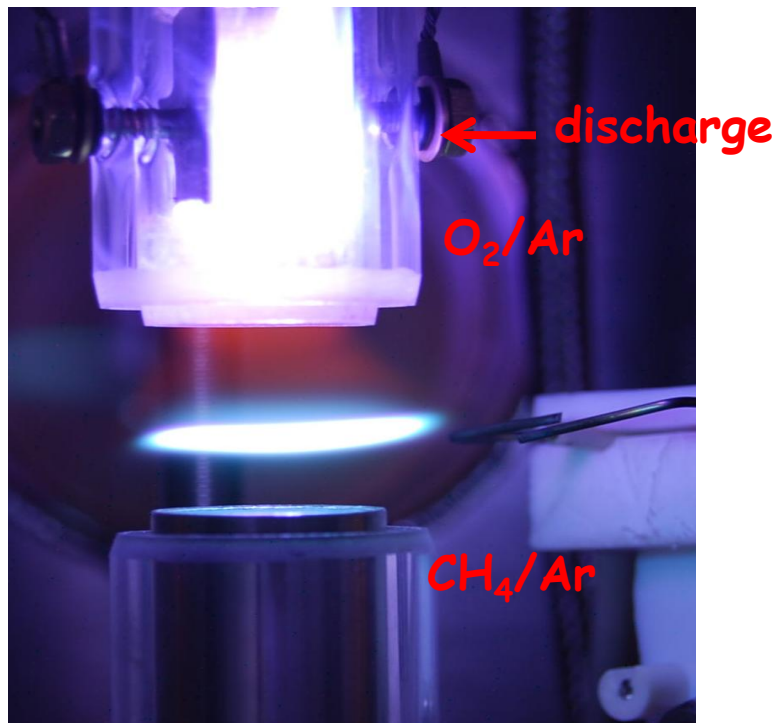


Energy Coupling Into Flow

$\approx 1$  eV to produce  $O_2(a^1\Delta_g)$

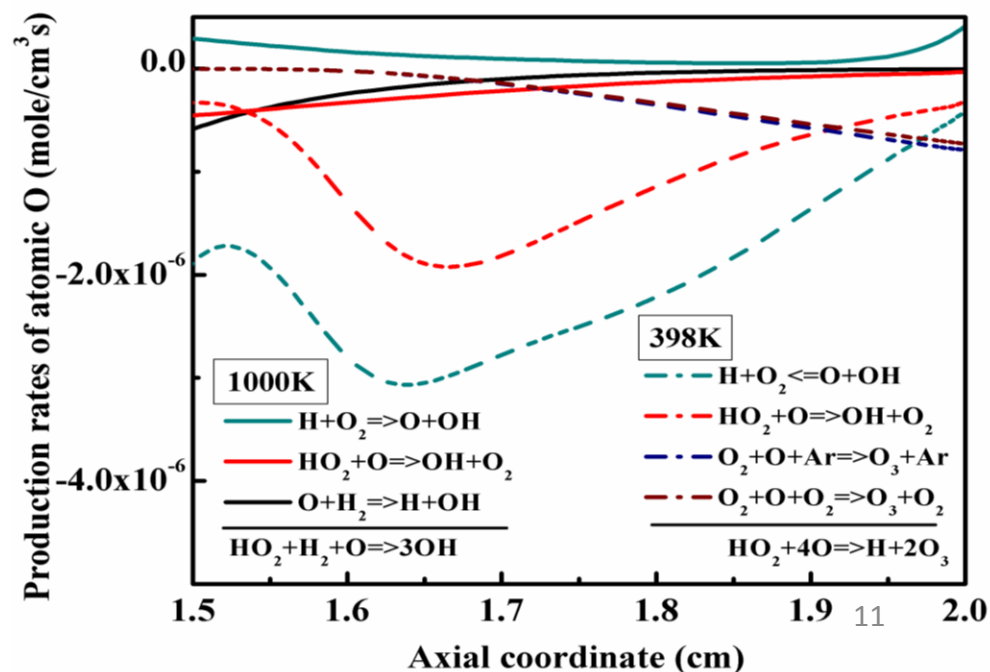
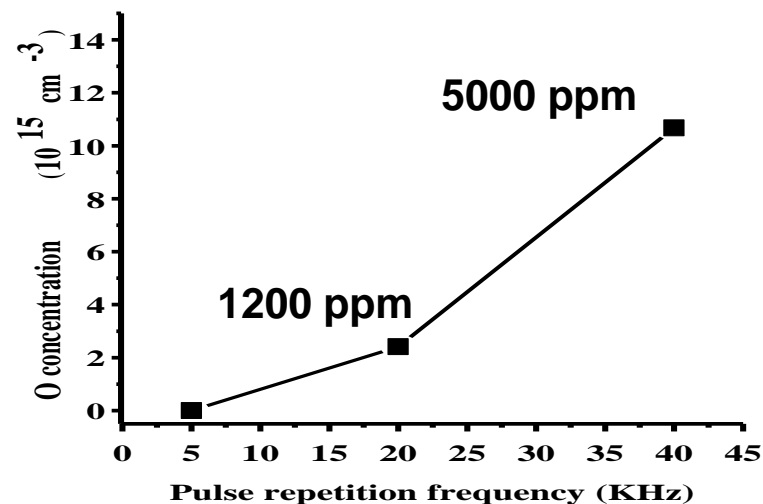


# Previous researches – Atomic oxygen effect



**Crossover T: 900 K**

**O quenched even at 60 Torr:  
How to utilize radicals efficiently?**





# Research focus in the second year

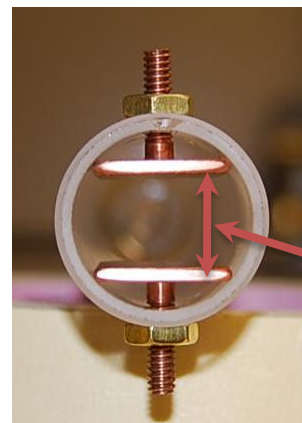
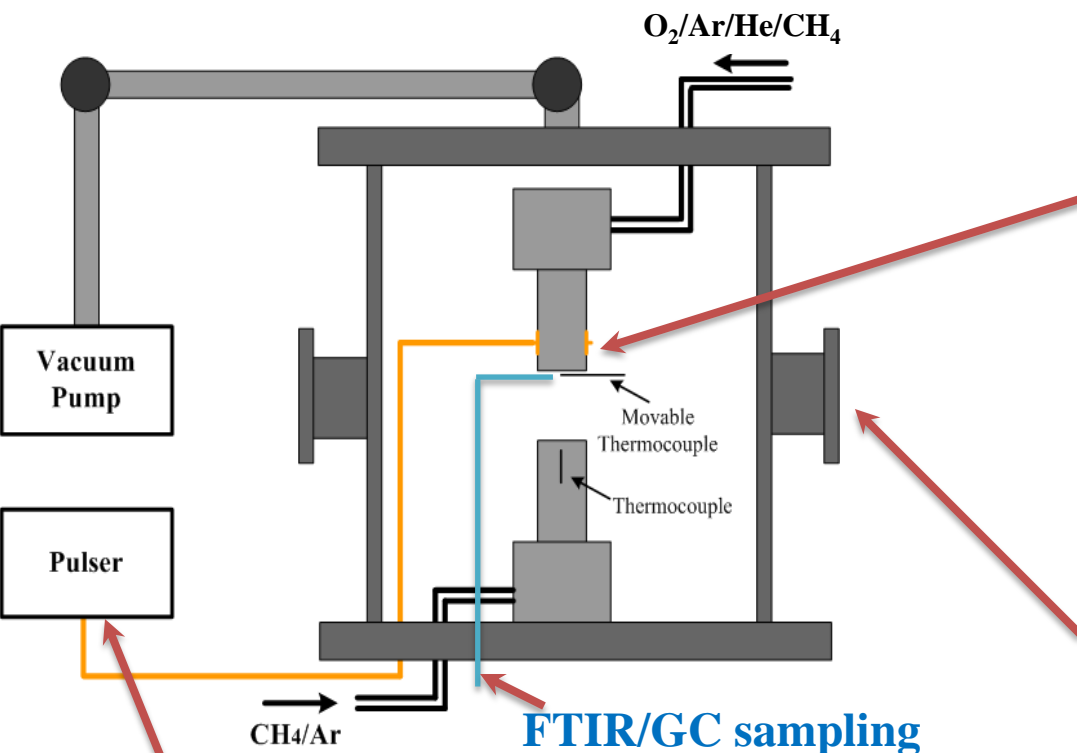
- Thrust 1. Kinetic effects of non-equilibrium plasma-assisted fuel oxidation on diffusion flame extinction limits**
- Thrust 2. Direct ignition and the S-curve transition by *in situ* nano-second pulsed discharge**
- Thrust 3. Plasma flame chemistry study in a flow reactor with Molecular Beam sampling Mass Spectrum (MBMS)**
- Thrust 4. Development of a plasma assisted jet stirred reactor with molecular beam sampling and a high pressure ignition chamber**



## **Thrust 1. Kinetic effects of non-equilibrium plasma-assisted fuel oxidation on diffusion flame extinction limits**

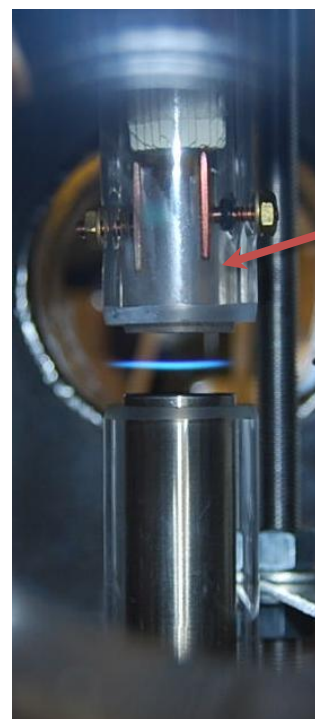


# Experimental setup



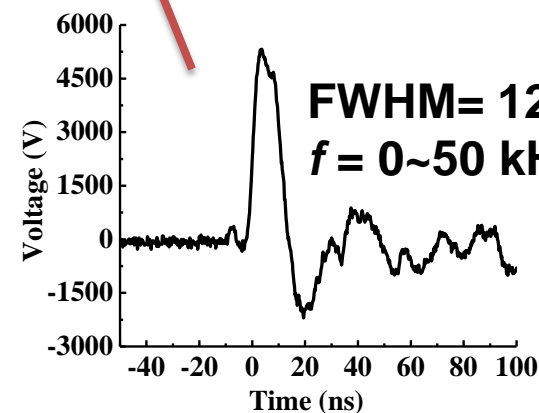
15 mm × 22 mm

10 mm



10 mm away from exit

20 & 28 mm ID



FWHM= 12 ns

$f = 0 \sim 50$  kHz

$E/N \sim 10^{-15} \text{ Vcm}^2$

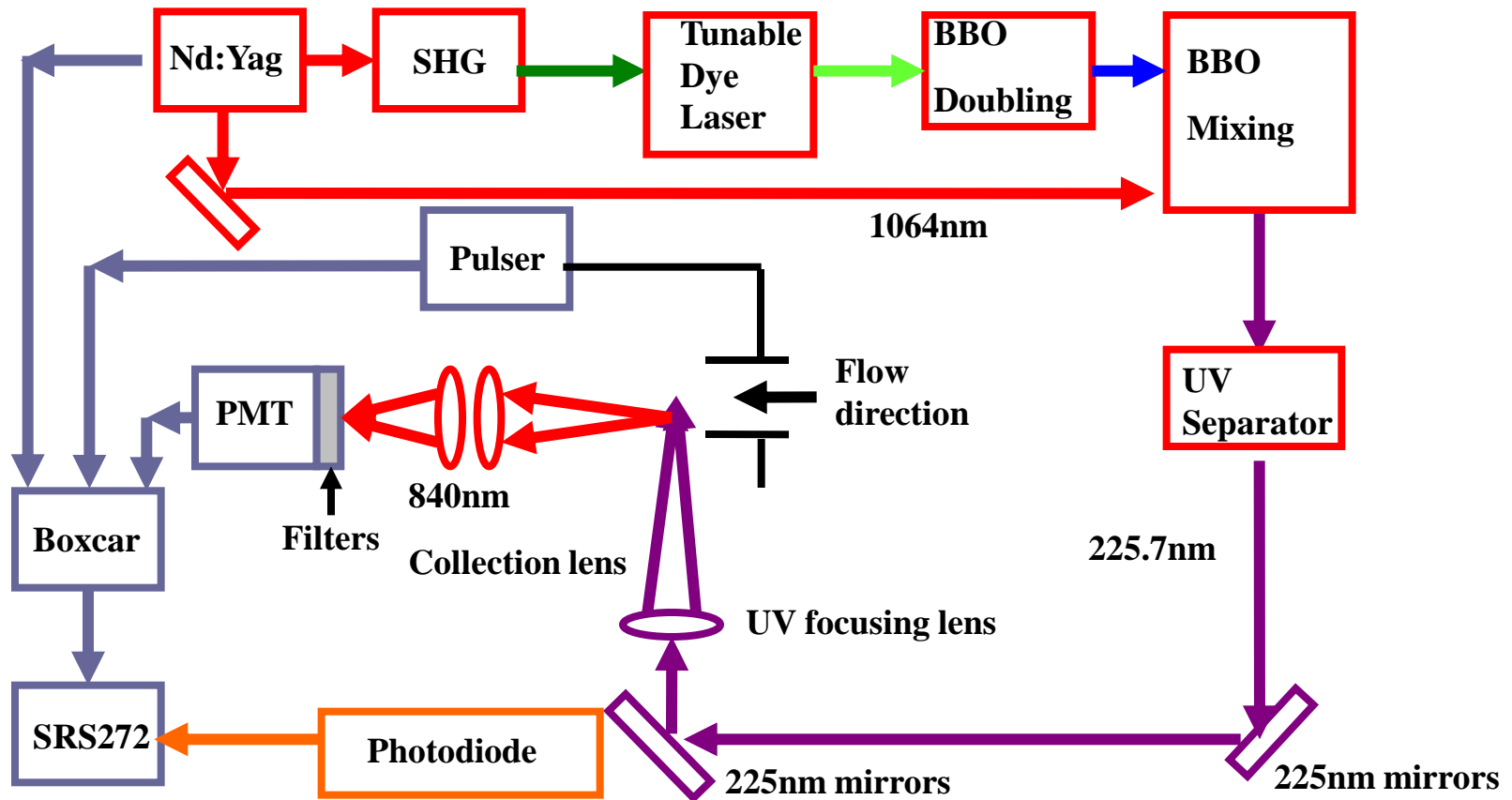
Power ~ 1.3 mJ/Pulse

**P = 60 Torr**

$$a_o = \frac{2U_o}{L} \left( 1 + \frac{U_f \sqrt{\rho_f}}{U_o \sqrt{\rho_o}} \right)$$



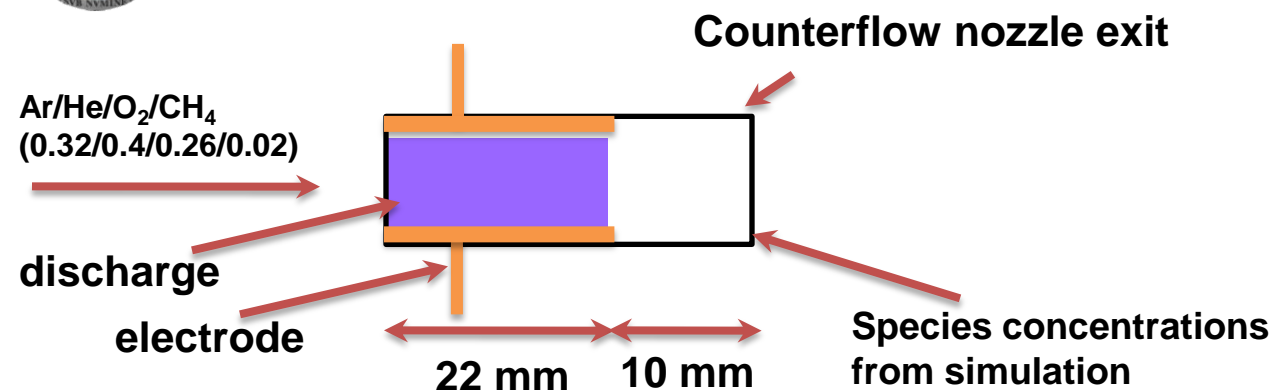
# Laser diagnostics schematic







# Numerical model



**Kinetic model:** OSU air plasma model [1,2] with USC mech II in addition of Ar/He/CH<sub>4</sub> related reactions.

**Physical model:** quasi-one-dimensional flow equation + steady two-term expansion Boltzmann equation [1]

Reactions [1-8]	Rate Const (cm <sup>3</sup> s <sup>-1</sup> )
$e + O_2 \rightarrow e + 2O$	$f(E/N)$
$e + O_2 \rightarrow e + O + O(D)$	$f(E/N)$
$e + CH_4 \rightarrow CH_3 + H + e$	$f(E/N)$
$e + Ar \rightarrow Ar^* + e$	$f(E/N)$
$e + Ar \rightarrow Ar(+) + 2e$	$f(E/N)$
$e + He \rightarrow He^* + e$	$f(E/N)$
$e + He \rightarrow He(+) + 2e$	$f(E/N)$
$Ar^* + CH_4 \rightarrow Ar + CH_2 + 2H$	$3.3 \times 10^{-10}$
$Ar^* + CH_4 \rightarrow Ar + CH + H_2 + H$	$5.8 \times 10^{-10}$

Reactions	Rate Const (cm <sup>3</sup> s <sup>-1</sup> )
$Ar(+) + CH_4 \rightarrow Ar + CH_3(+) + H$	$6.5 \times 10^{-10}$
$Ar(+) + CH_4 \rightarrow Ar + CH_2(+) + H_2$	$1.4 \times 10^{-10}$
$Ar^* + CH_4 \rightarrow Ar + CH_3 + H$	$5.8 \times 10^{-10}$
$Ar^* + CH_4 \rightarrow Ar + CH_2 + H_2$	$5.8 \times 10^{-10}$
$He(+) + O_2 \rightarrow O(+) + O + He$	$0.6 \times 10^{-11} T^{0.5}$
$Ar^* + O_2 \rightarrow Ar + 2O$	$2 \times 10^{-10}$
$He(+) + O_2(a) \rightarrow O(+) + O + He$	$0.6 \times 10^{-11} T^{0.5}$
$He + 2O \rightarrow He^* + O_2$	$1 \times 10^{-33}$
$He^* + CH_4 \rightarrow CH + H_2 + H + He$	$5.6 \times 10^{-13}$

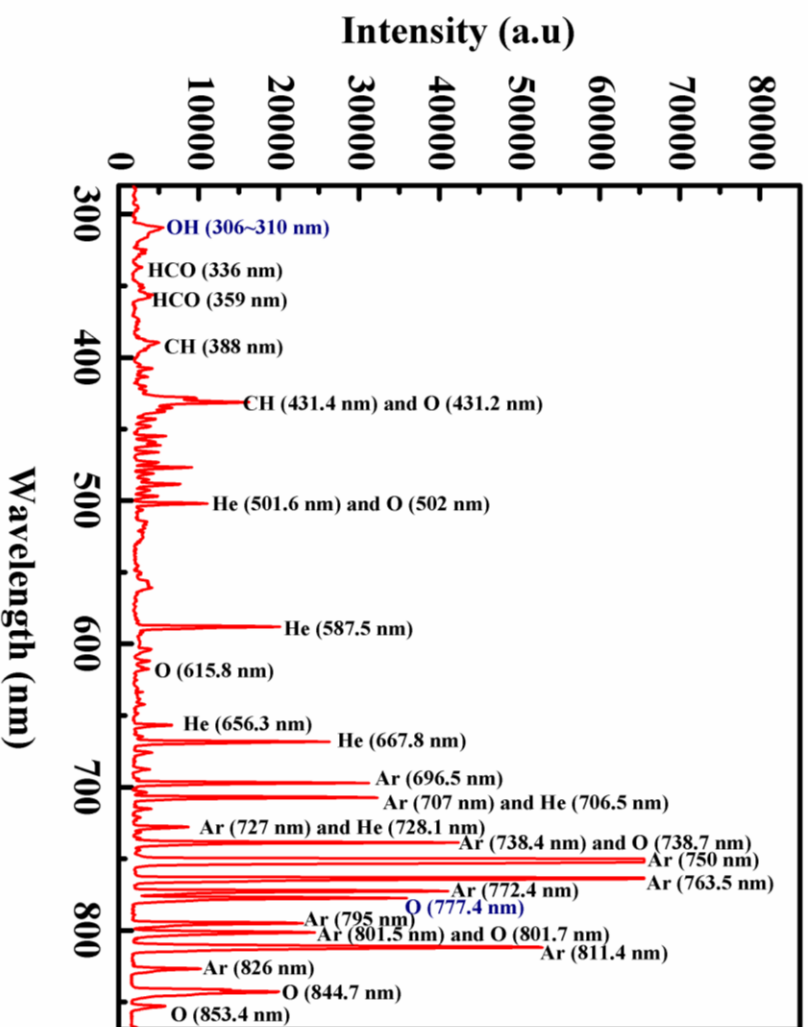
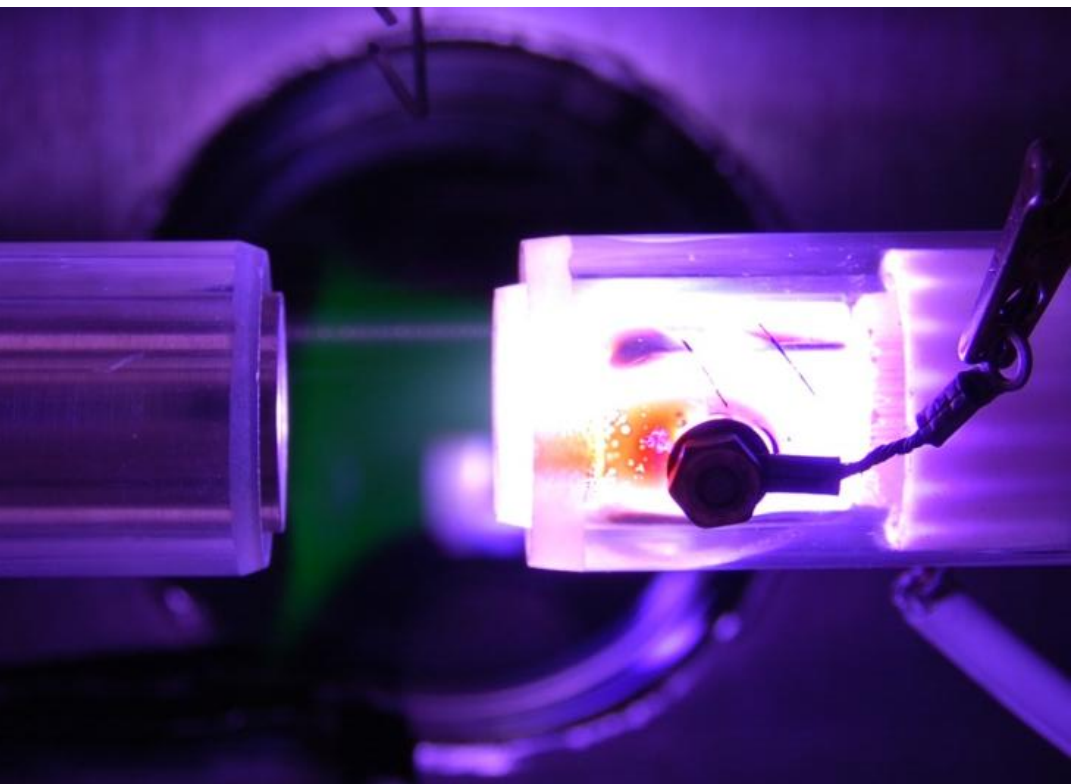
Reference:

[1]. A. Bao, Ph.D thesis (2008) OSU [2]. M. Uddi et al, PCI 32(2009) 929 [3]. I.N. Kosarov et al, C&F 156(2009) 221 [4]. A. Hicks et al, JPD, 38(2005) 3812 [5]. D. S. Stafford et al, JAP, 96(2004) 2451 [6]. M. Tsuji et al, JCP, 94(1991) 277 [7]. A.M. Starik et al, C&F, 157(2010) 313 [8]. I.N. Kosarev et al, C&F 154(2008) 569



# Experimental observations of discharges

$\text{O}_2(0.26)/\text{Ar}(0.32)/\text{He}(0.4)/\text{CH}_4(0.02)$



**Strongest emission:  $\text{Ar}^*$ ,  $\text{O}^*$**

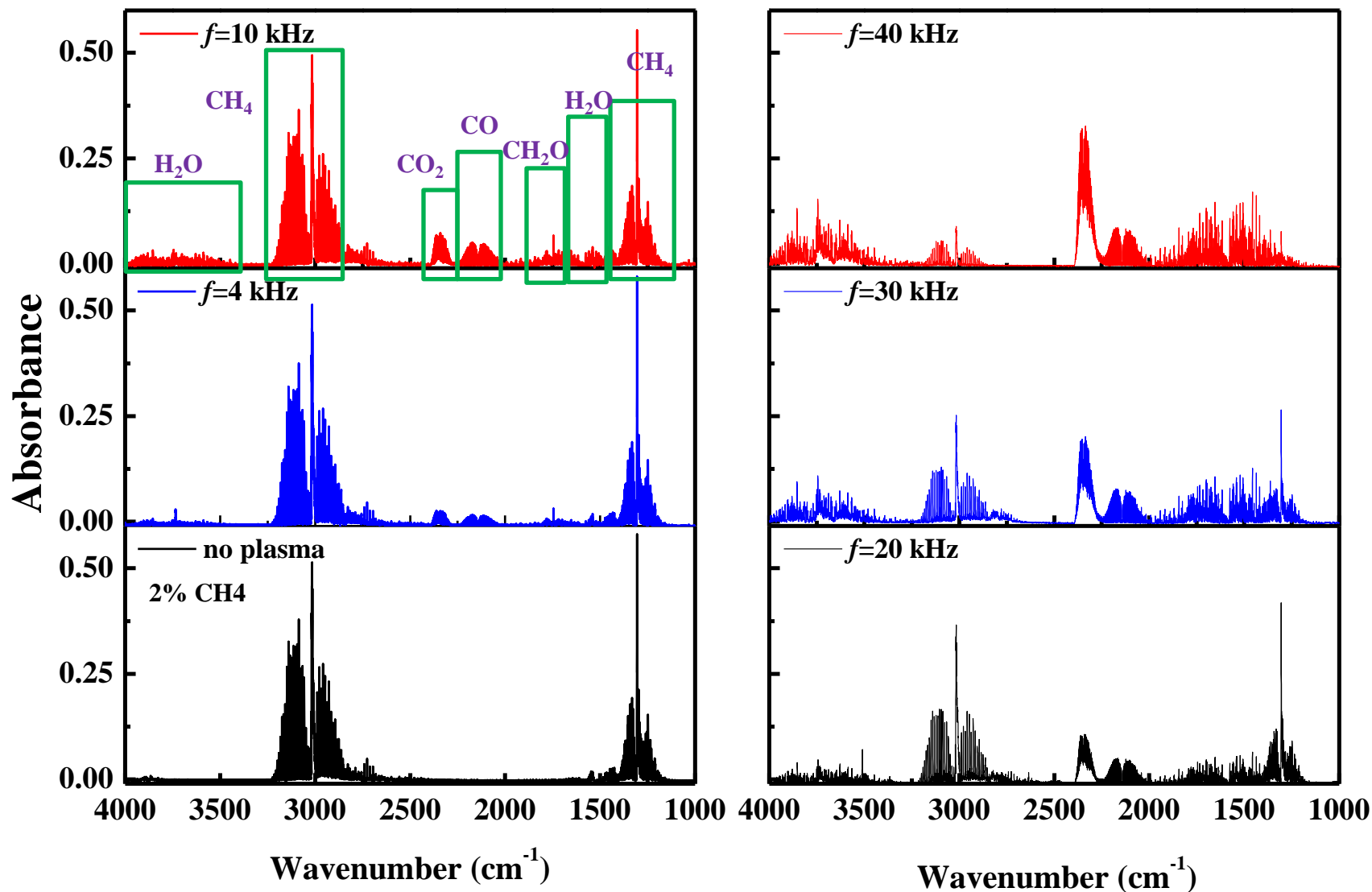
**Emissions:  $\text{He}^*$ ,  $\text{OH}^*$ ,  $\text{HCO}^*$ , and  $\text{CH}^*$**

$f=30 \text{ kHz}$



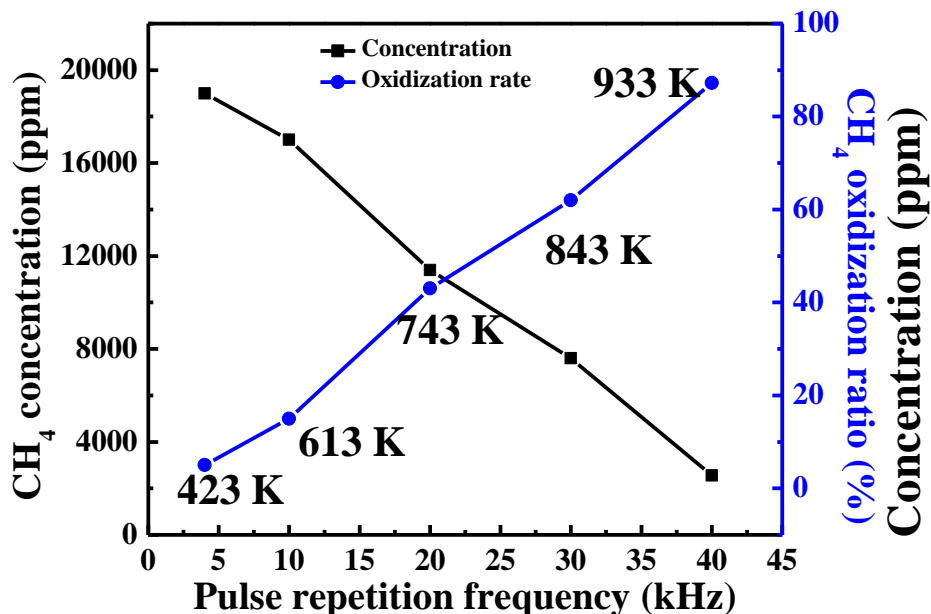
## Discharge repetition effect on species concentrations

### FTIR spectrum with different pulse frequency

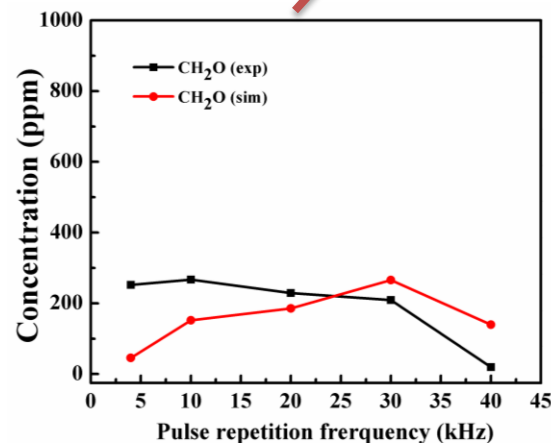
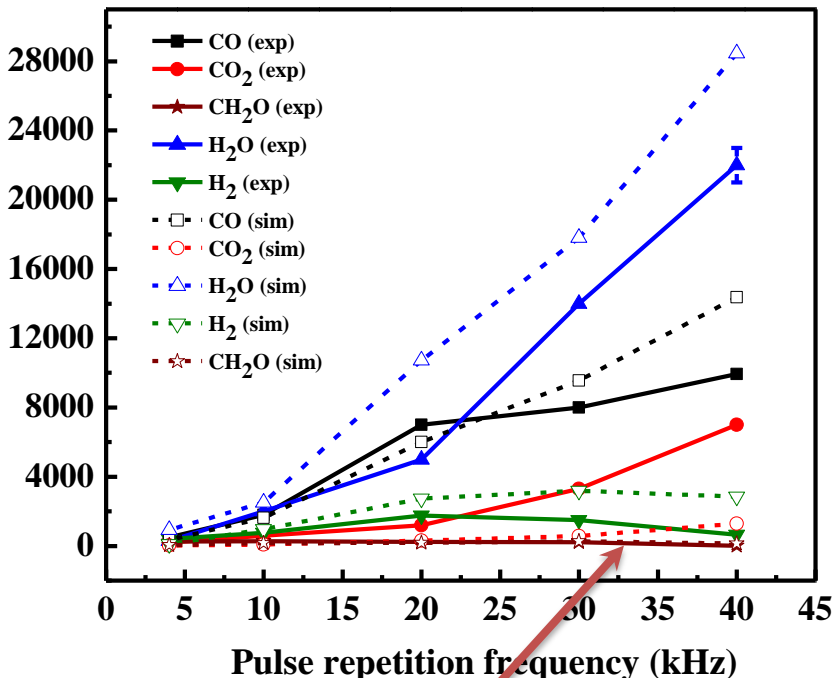




# Discharge repetition effect on species concentrations



Under prediction: CO<sub>2</sub>  
Over prediction: CO, H<sub>2</sub>, H<sub>2</sub>O



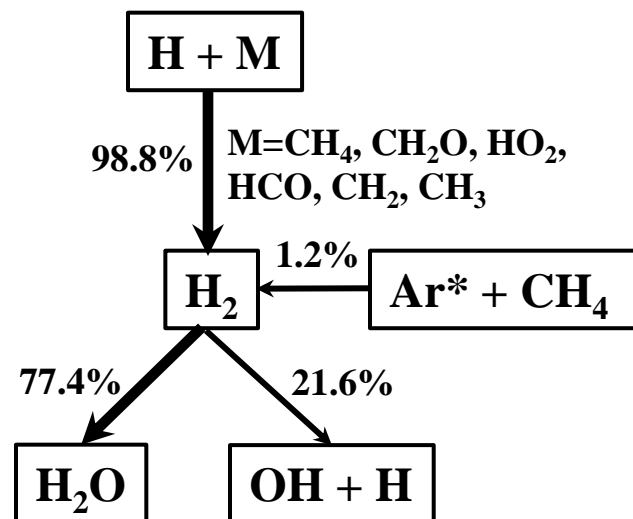
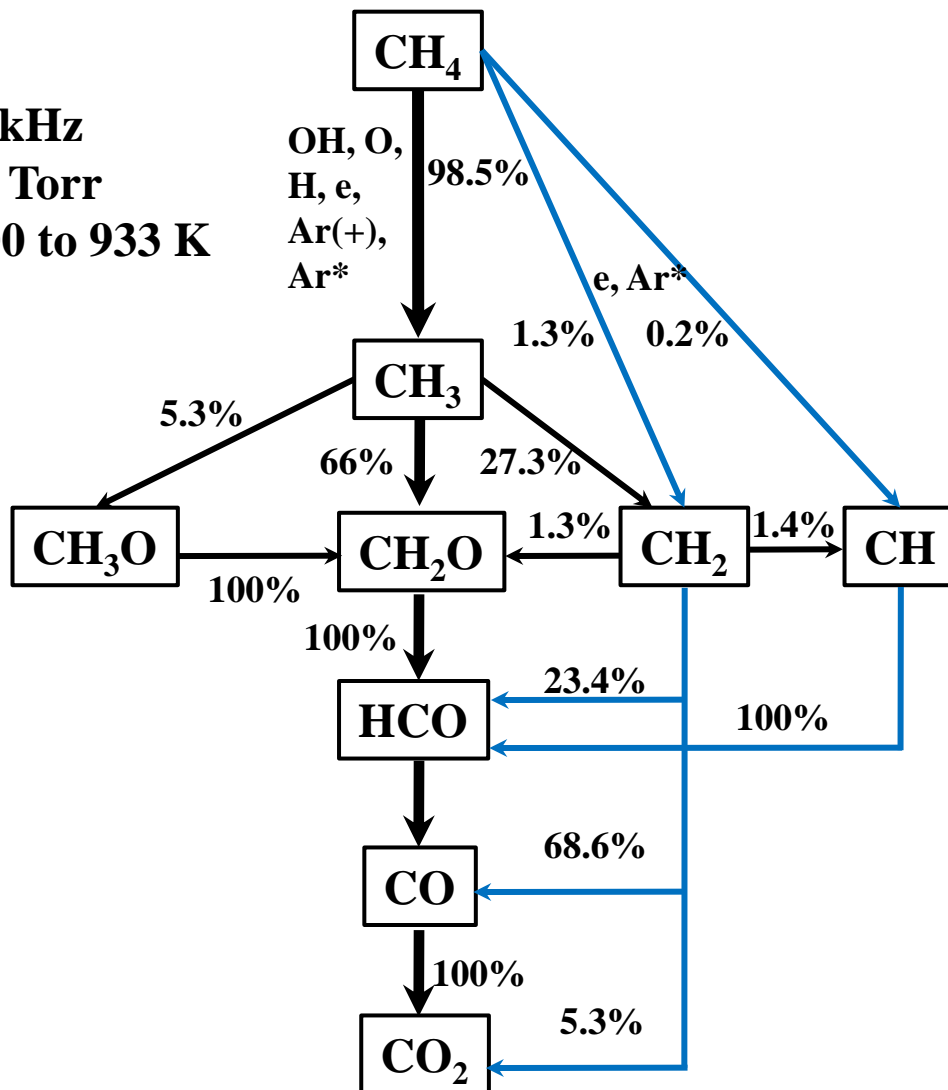
Carbon deficiency: 5%  
Relative uncertainties:  
<1% for CH<sub>4</sub>, CO, CO<sub>2</sub>  
5% for H<sub>2</sub>O and H<sub>2</sub>

The uncertainty of CH<sub>2</sub>O measurement is 80 ppm



# Reaction path analysis-CH<sub>4</sub>&H<sub>2</sub>

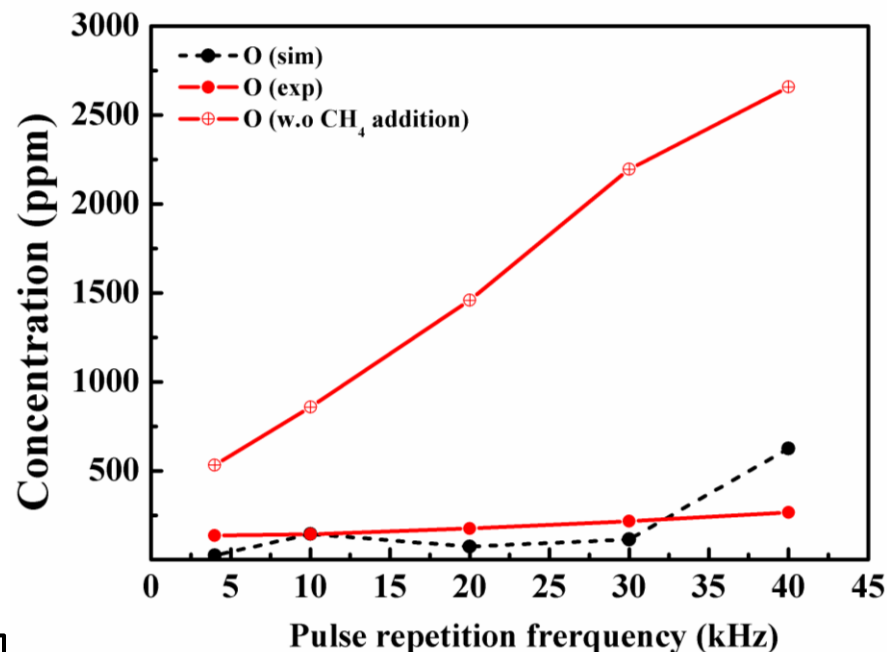
$f = 40$  kHz  
 $P = 60$  Torr  
 $T = 300$  to  $933$  K





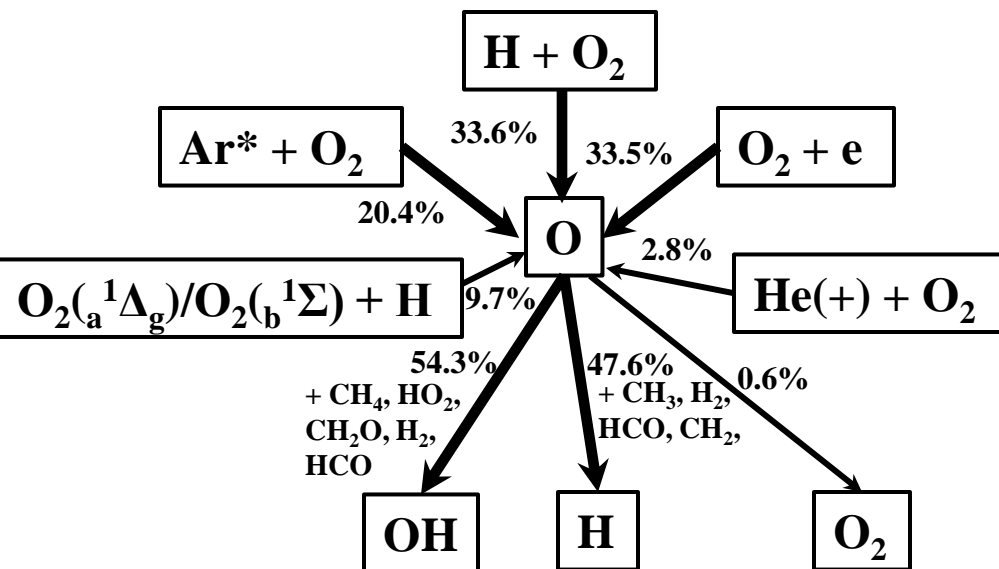
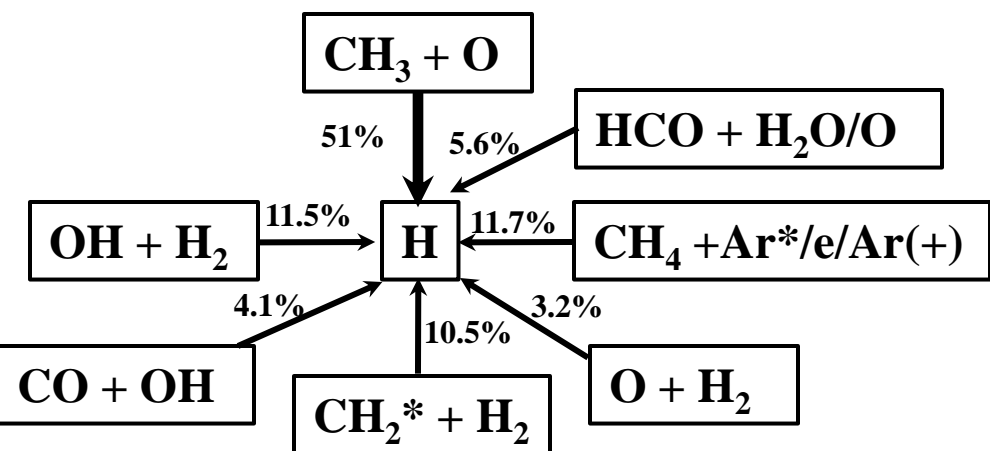
# Reaction path analysis-H&O

$f = 40 \text{ kHz}$   
 $P = 60 \text{ Torr}$   
 $T = 300 \text{ to } 933 \text{ K}$



Mechanism was not validated below 700 K  
 Large uncertainty at low temperature

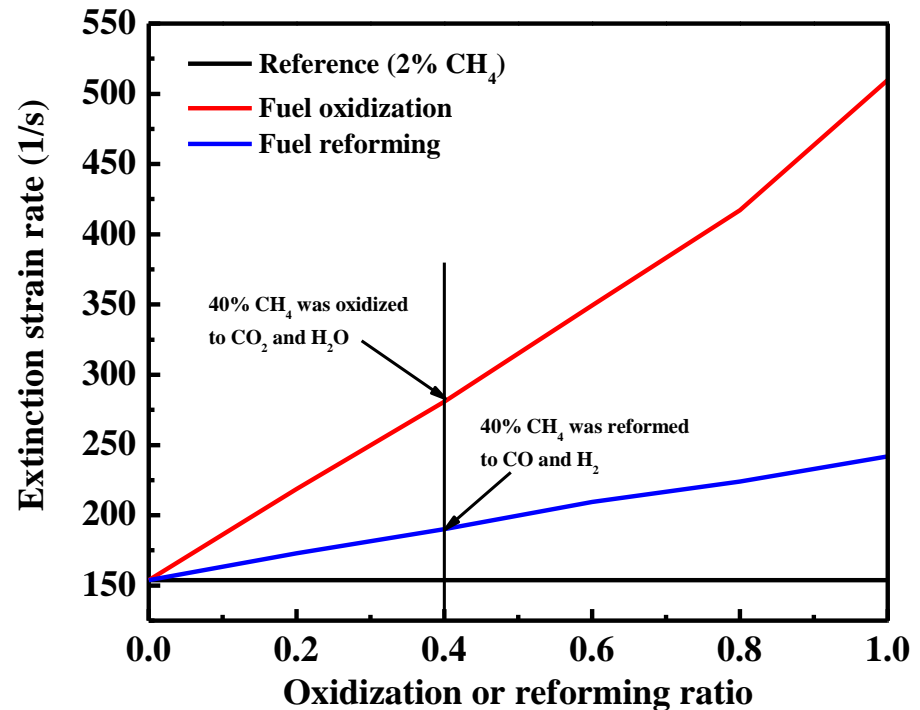
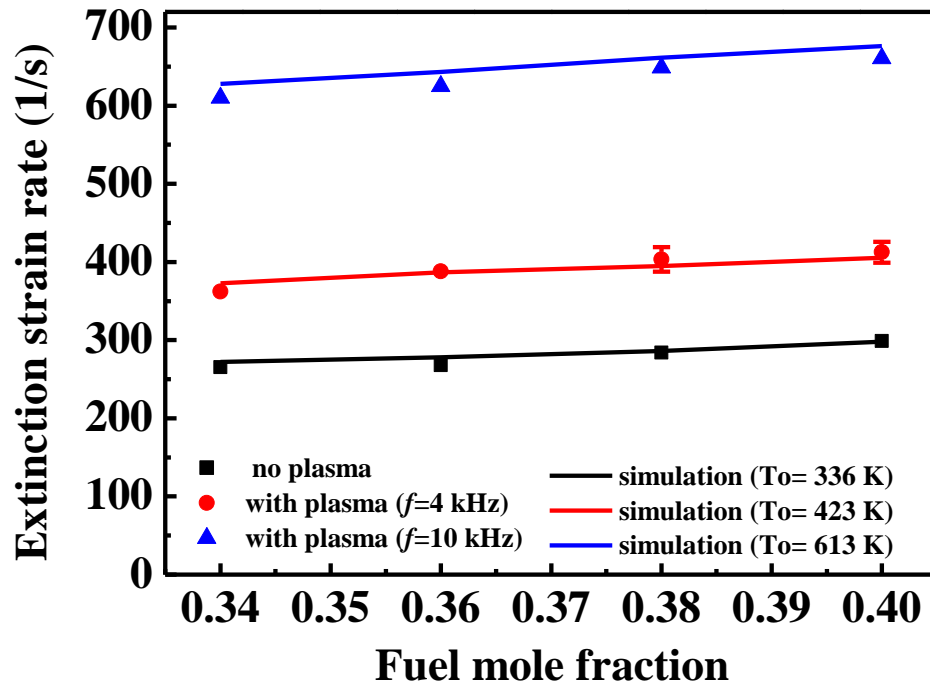
the reaction rate at 300 K for  
 $O(^1D) + H_2 = H + OH$  ( $4.4 \times 10^{10} / \text{cm}^3 \text{s}$ )  
 is much larger than  
 $O + H_2 = H + OH$  ( $2.6 \times 10^3 / \text{cm}^3 \text{s}$ ). 21





# Extinction limit measurement & calculation

Faster fuel oxidization, larger extinction extension



Simulations were performed with experimentally measured boundary conditions.

OH, H concentrations were estimated from simulation by matching O concentrations.

Case 1: fuel was oxidized to  $\text{CO}_2$  &  $\text{H}_2\text{O}$

Case 2: fuel was reformed to  $\text{CO}$  &  $\text{H}_2$

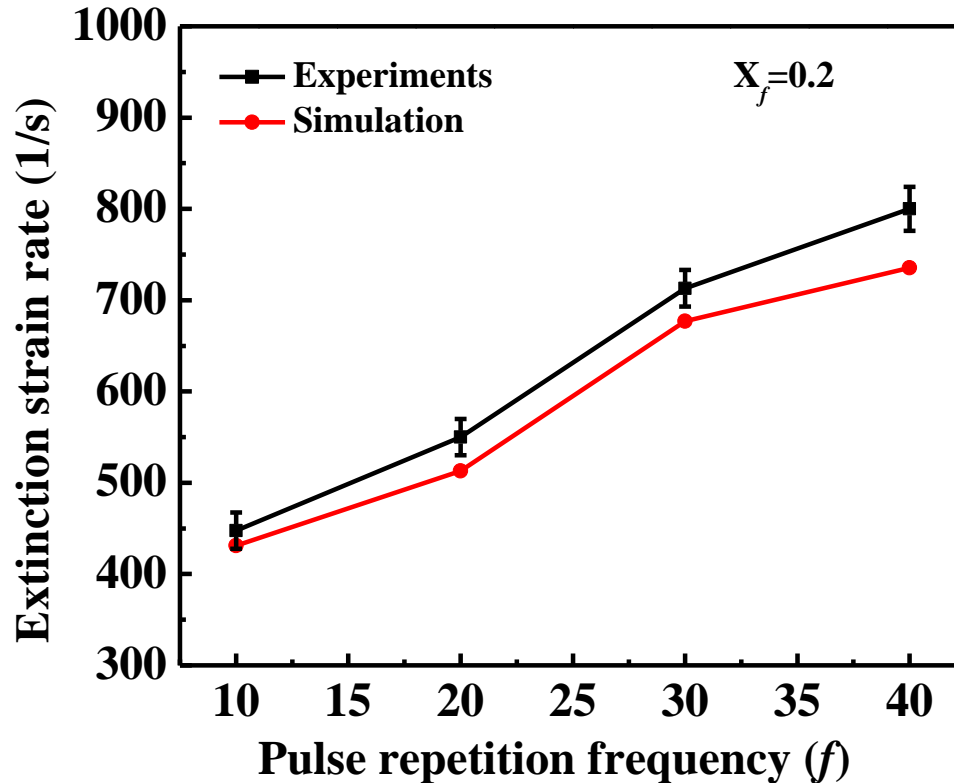
Fuel reforming enhancement: fast  $\text{H}_2$  chemistry

Fuel oxidization enhancement: extracting chemical enthalpy rapidly



# Extinction limit measurement & calculation

$\text{CH}_4$  oxidization ratio (or  $f$ ) increased, extinction limits increased significantly



5.3% enhancement from  $\text{H}_2$

The dominant enhancement mechanism is plasma introduced rapid fuel oxidization.

Deviation is due to additional reaction paths, but not significant (10%).

Simulations were performed with experimentally measured boundary conditions.

$\text{OH}$ ,  $\text{H}$  concentrations were estimated from simulation by matching  $\text{O}$  concentrations.

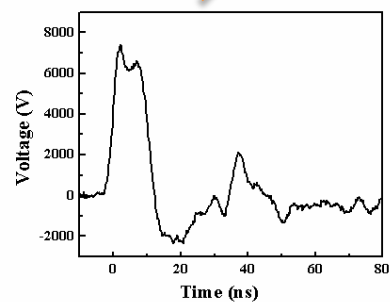
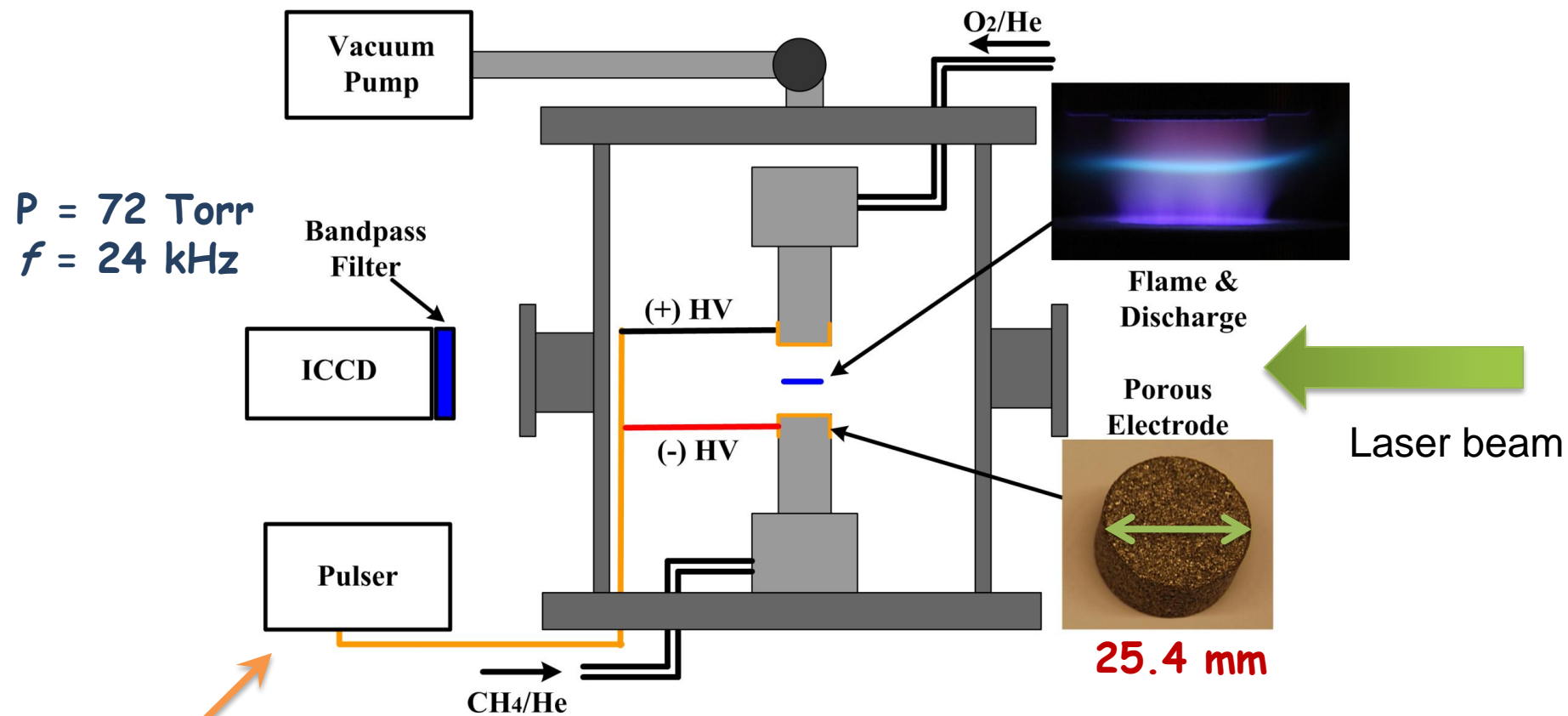




## **Thrust 2. Direct ignition and the S-curve transition by *in situ* nano-second pulsed discharge**



# Experimental setup

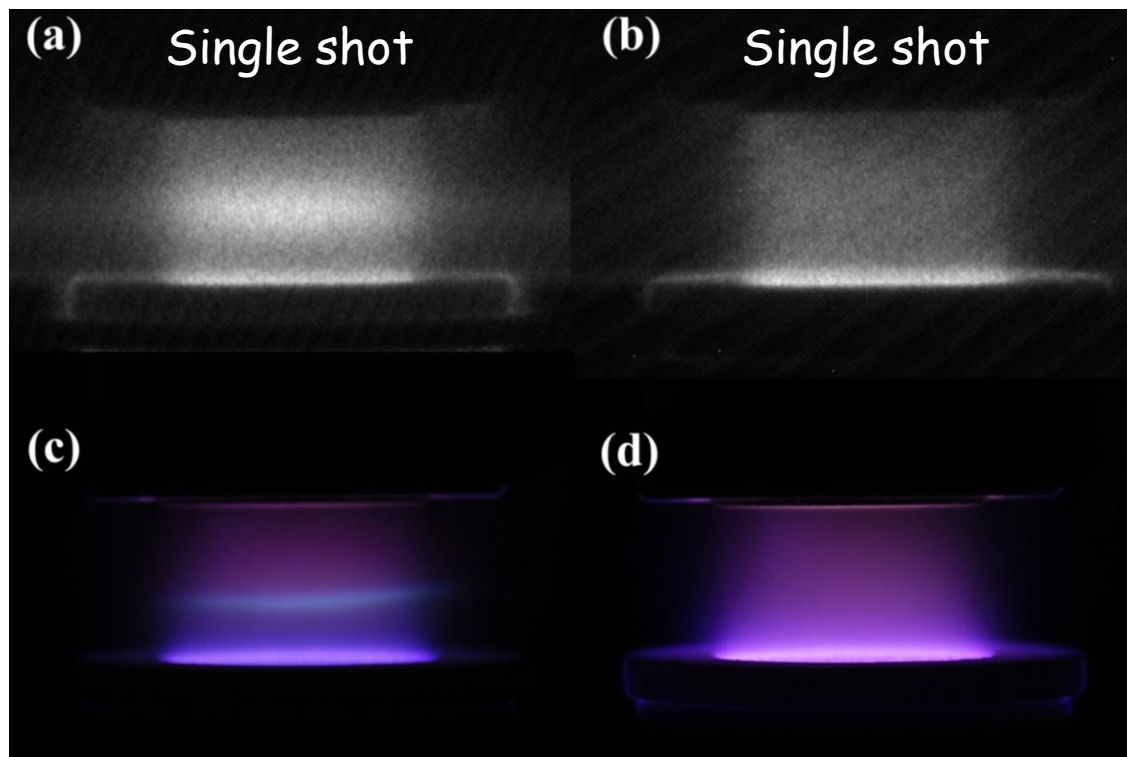
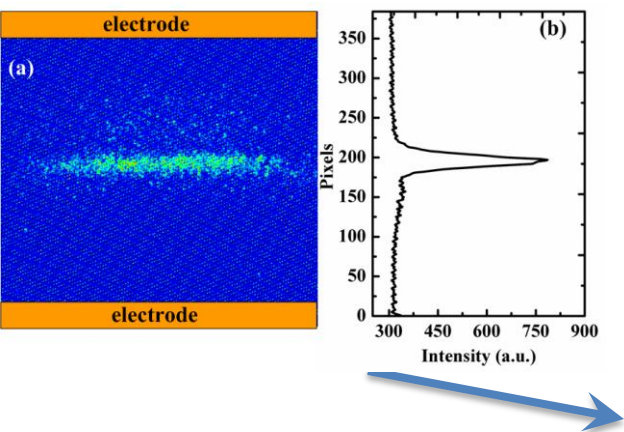


Power ~ 17 W



# ICCD images

**OH\* emission ~310 nm**  
**30  $\mu$ s gate**

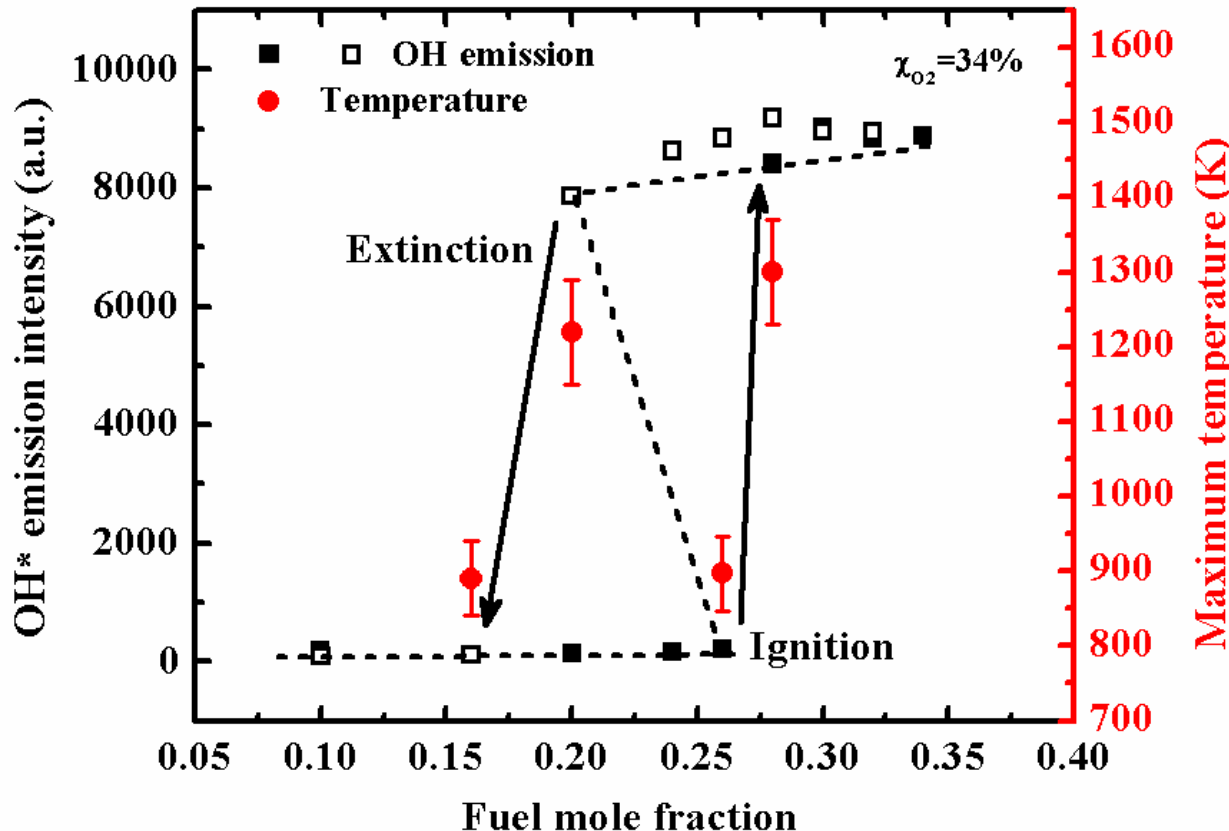


- (a) ICCD image, He/O<sub>2</sub> (0.6:0.4) and He/CH<sub>4</sub> (0.75:0.25), 50 ns gate  
(b) ICCD image, He/O<sub>2</sub> (0.6:0.4) and He/CH<sub>4</sub> (0.86:0.14), 50 ns gate  
(c) direct photo of (a), 50 ms exposure time  
(d) direct photo of (b), 50 ms exposure time  
P = 72 Torr, f = 24 kHz, a = 175 1/s



# Classical S-curve

hysteresis between ignition and extinction: S curve



Rayleigh Scattering<sup>[1,2]</sup>  
method for T  
measurement at 532  
nm from Nd:YAG laser

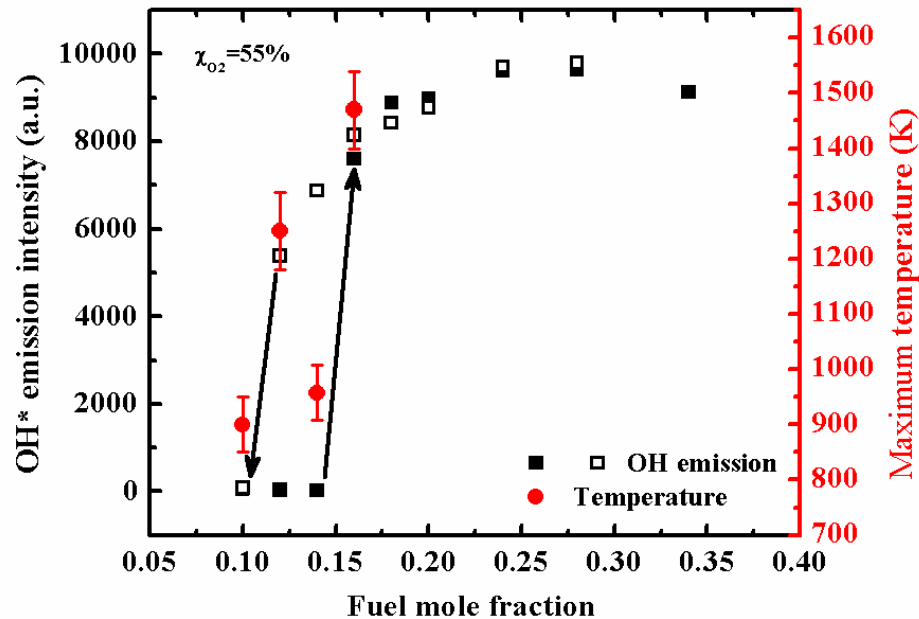
Relationship between OH\* emission intensity, local maximum temperature and fuel mole fraction,  $T_0 = 650$  K,  $T_f = 600$  K He/O<sub>2</sub> = 0.66:0.34,  $P = 72$  Torr,  $f = 24$  kHz,  $a = 400$  1/s



# S curve transition

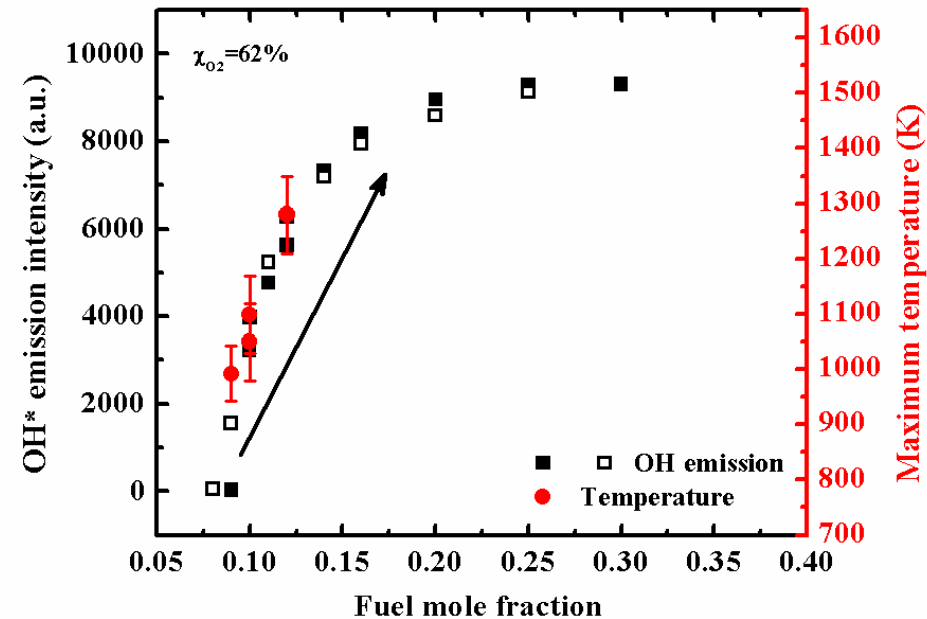
Relationship between  $\text{OH}^*$  emission intensity, local maximum temperature and fuel mole fraction,  $P = 72 \text{ Torr}$ ,  $f = 24 \text{ kHz}$ ,  $a = 400 \text{ 1/s}$

$\text{He}/\text{O}_2 = 0.45:0.55$



ignition and extinction points were pushed to lower fuel concentrations

$\text{He}/\text{O}_2 = 0.38:0.62$



monotonic ignition and extinction curve (monotonic S curve)



# Numerical modeling

OPPDIF + electron impact

Kinetic mechanism: USC mech II + OSU air plasma model<sup>[1]</sup>

<b>e + O<sub>2</sub> reactions</b>	<b>Rate (cm<sup>3</sup>s<sup>-1</sup>)</b>
$e + O_2 \rightarrow 2O + e$	$f(E/N)$
$e + O_2 \rightarrow O + O(D) + e$	$f(E/N)$
$e + O_2 \rightarrow O_2(+) + 2e$	$f(E/N)$
$e + O_2 \rightarrow O_2(a) + e$	$f(E/N)$

<b>e + CH<sub>4</sub> reactions</b>	<b>Rate (cm<sup>3</sup>s<sup>-1</sup>)</b>
$e + CH_4 \rightarrow CH_3 + H + e$	$f(E/N)$
$e + CH_4 \rightarrow CH_2 + H_2 + e$	$f(E/N)$
$e + CH_4 \rightarrow CH_4(+) + 2e$	$f(E/N)$

<b>He related reactions</b>	<b>Rate (cm<sup>3</sup>s<sup>-1</sup>)</b>
$He + e \rightarrow He^* + e$	$f(E/N)$
$He + e \rightarrow He(+) + 2e$	$f(E/N)$
$He^* + O_2 \rightarrow O_2(+) + He + e$	$1.5 \times 10^{-11} T^{0.5}$
$He(+) + O_2 \rightarrow O(+) + O + He$	$0.6 \times 10^{-11} T^{0.5}$
$He^* + CH_4 \rightarrow CH + H_2 + H + He$	$5.6 \times 10^{-13}$

<b>Recombination reactions</b>	<b>Rate (cm<sup>3</sup>s<sup>-1</sup>)</b>
$e + O_2(+) \rightarrow 2O$	$5.6 \times 10^{-6} T^{-0.5}$
$He(+) + e + M \rightarrow He + M$	$1.4 \times 10^{-8}$
$e + O_2 + M \rightarrow O_2(-) + M$	$4.2 \times 10^{-27} T^{-1}$
$e + CH_4(+) \rightarrow CH_3 + H$	$1.0 \times 10^{-8}$

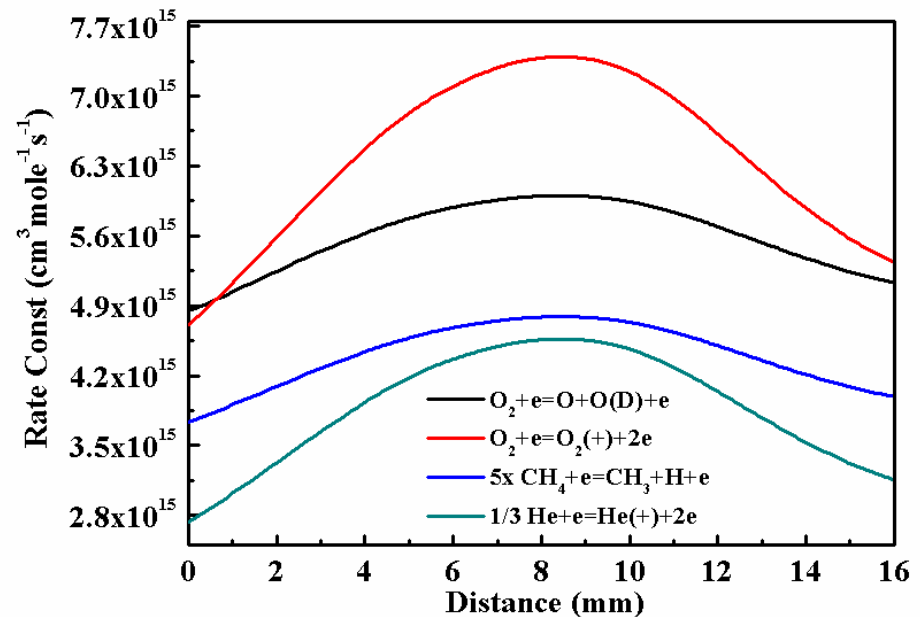
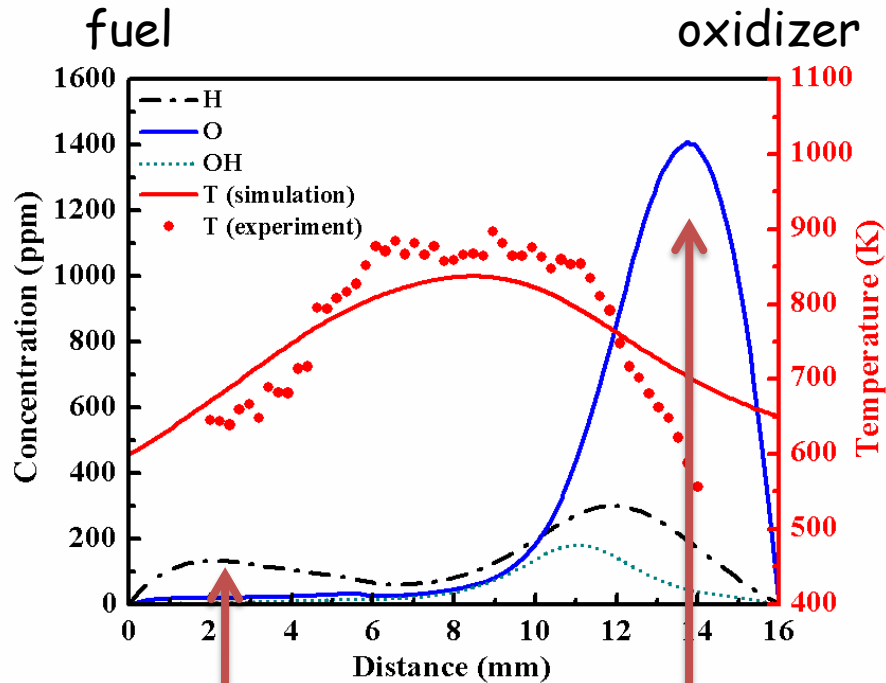
E: electric field, N: particle density

Rate constants: Boltzmann equation solver<sup>[1, 2]</sup>



# Simulation results

$X_{O_2} = 0.34$ ,  $X_{CH_4} = 0.16$ ,  $P = 72$  Torr,  $f = 24$  kHz,  $\alpha = 400$  1/s

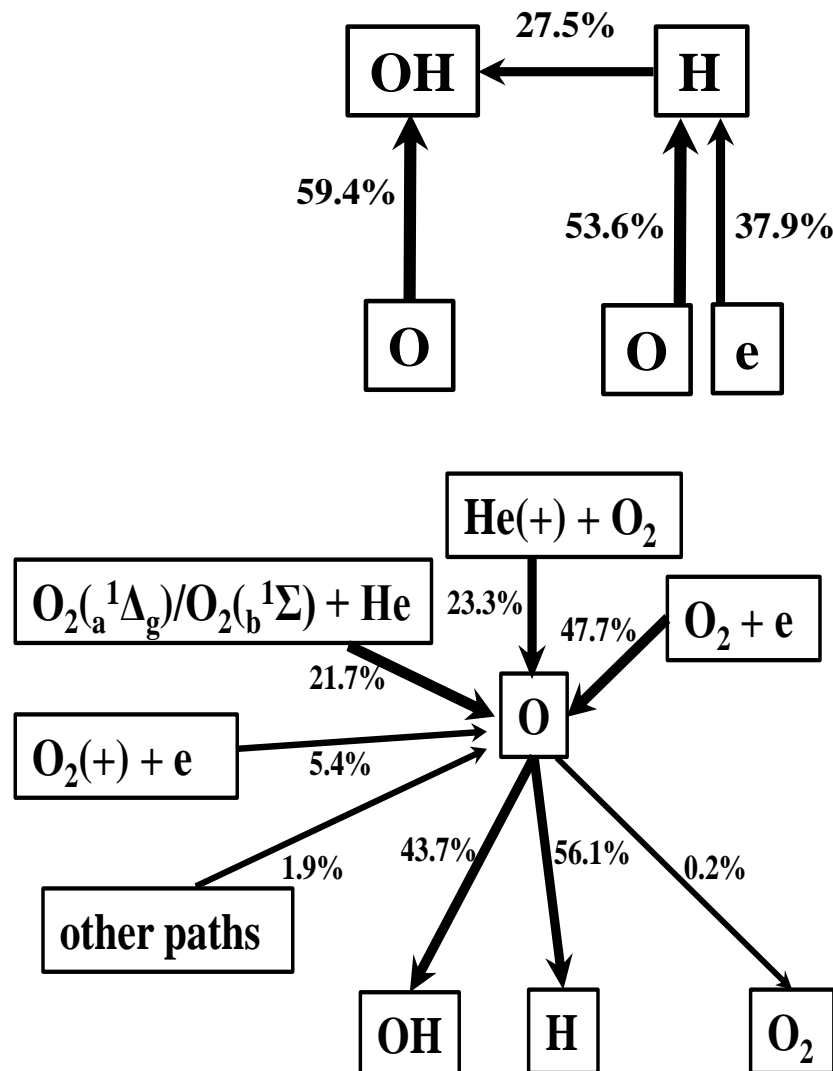
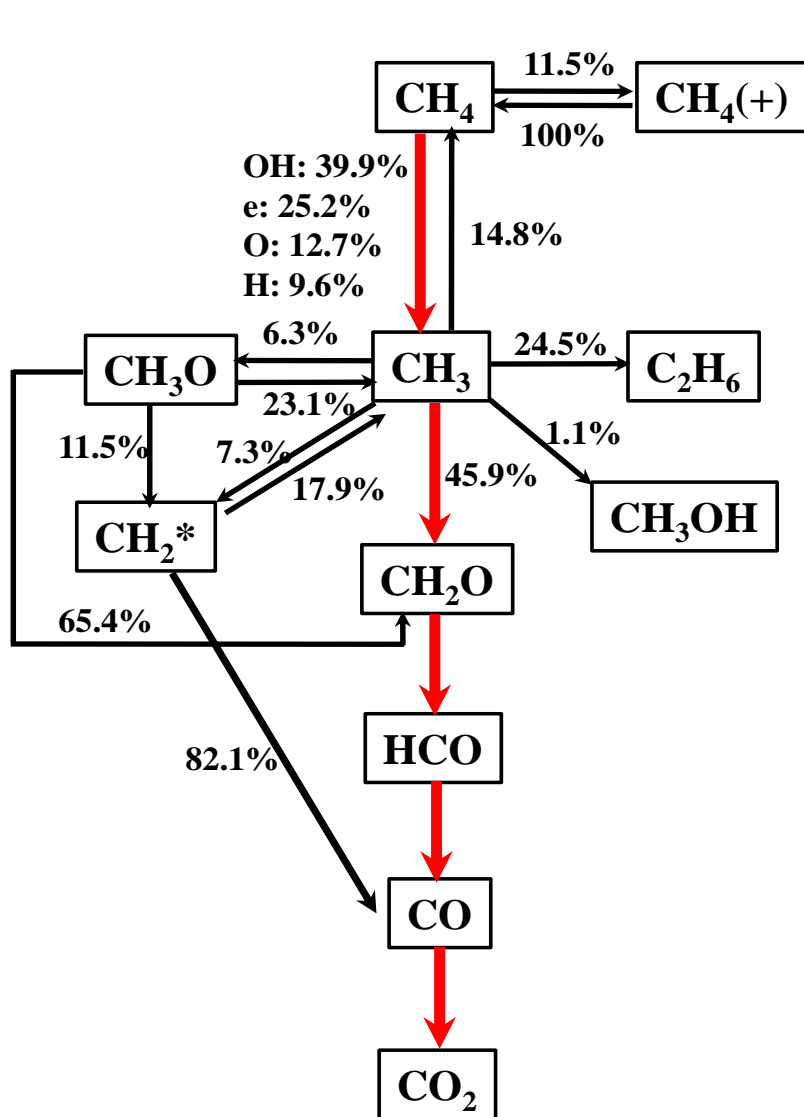


In situ discharge, increased  $T$ ,  
increased  $E/N$ , increased rate const

no flame, but reaction zone was built up by radicals generated from plasma



# Path flux analysis





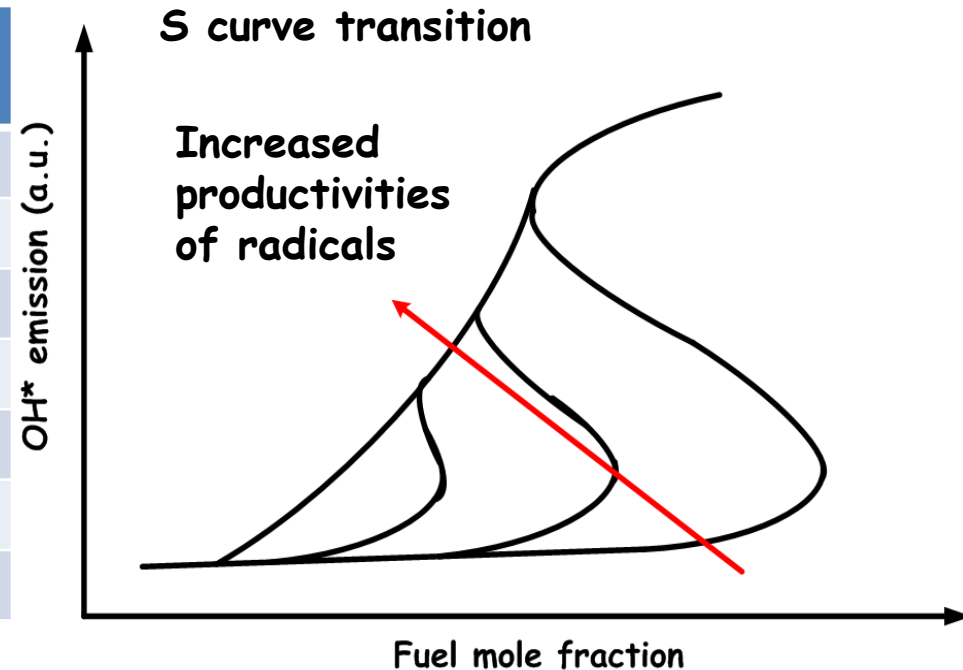


# Change of branching ratio

**Change of the branching ratio at the reaction zone!**

Reactions	Normalized branching ratio
$\text{H} + \text{O}_2 = \text{O} + \text{OH}$	1
$\text{e} + \text{O}_2 = \text{O} + \text{O}(\text{D}) + \text{e}$	0.48
$\text{e} + \text{O}_2 = \text{O} + \text{O}(+) + \text{e}$	0.42
$\text{e} + \text{CH}_4 = \text{CH}_3 + \text{H} + \text{e}$	0.22
$\text{He}(+) + \text{O}_2 = \text{O} + \text{O}(+) + \text{He}$	0.52
$\text{e} + \text{O}_2 = 2\text{O} + \text{e}$	0.06
$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	0.2

**1.7**



**76% of O production by e and ions from plasma**

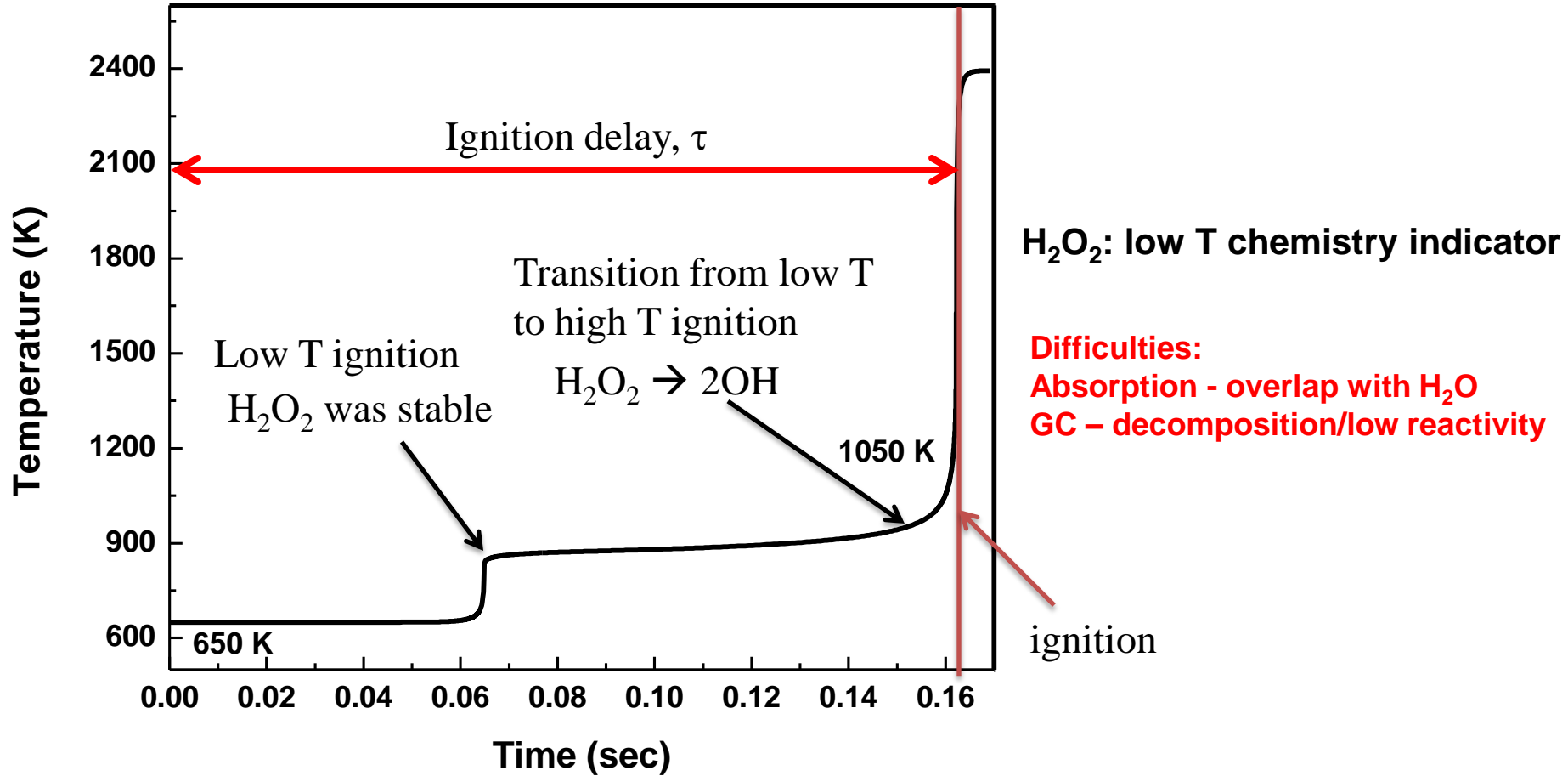
**Radical generation initiated the reaction zone and controlled the transition!!**



## **Thrust 3. Plasma flame chemistry study in a flow reactor with Molecular Beam sampling Mass Spectrum (MBMS)**



# Characteristic of low T chemistry



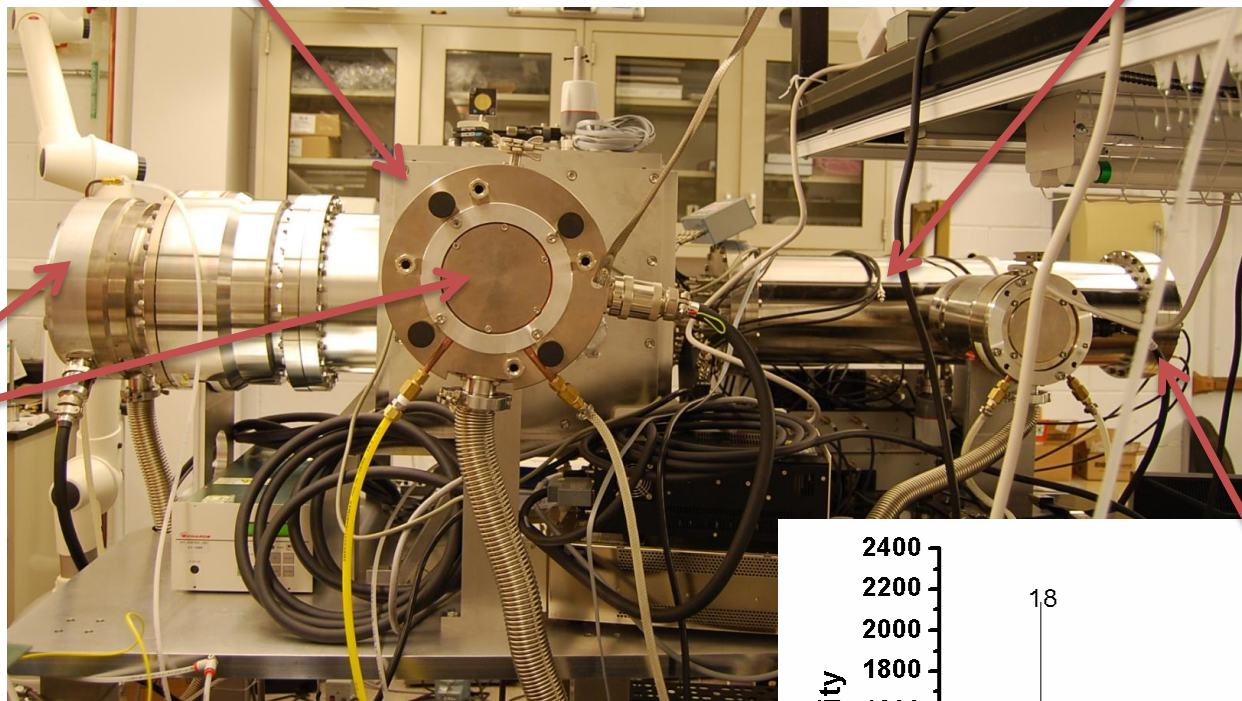


# Molecular Beam Mass Spectrum

**Sampling system**

**Time of fly**

**pump**



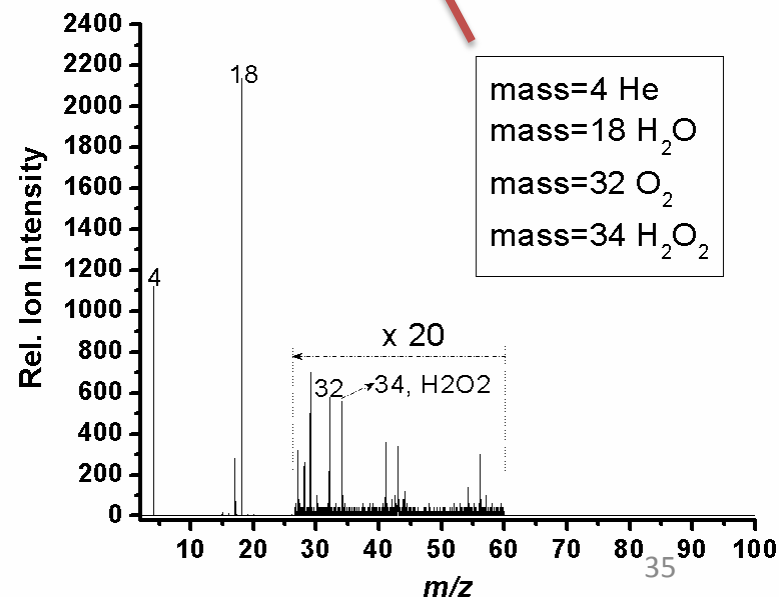
$$\frac{S_1}{S_{He}} = \frac{D_1}{D_{He}} \times \frac{\sigma_1}{\sigma_{He}} \times \frac{\chi_1}{\chi_{He}}$$

$S$  : signal intensity

$D$  : mass discrimination factor

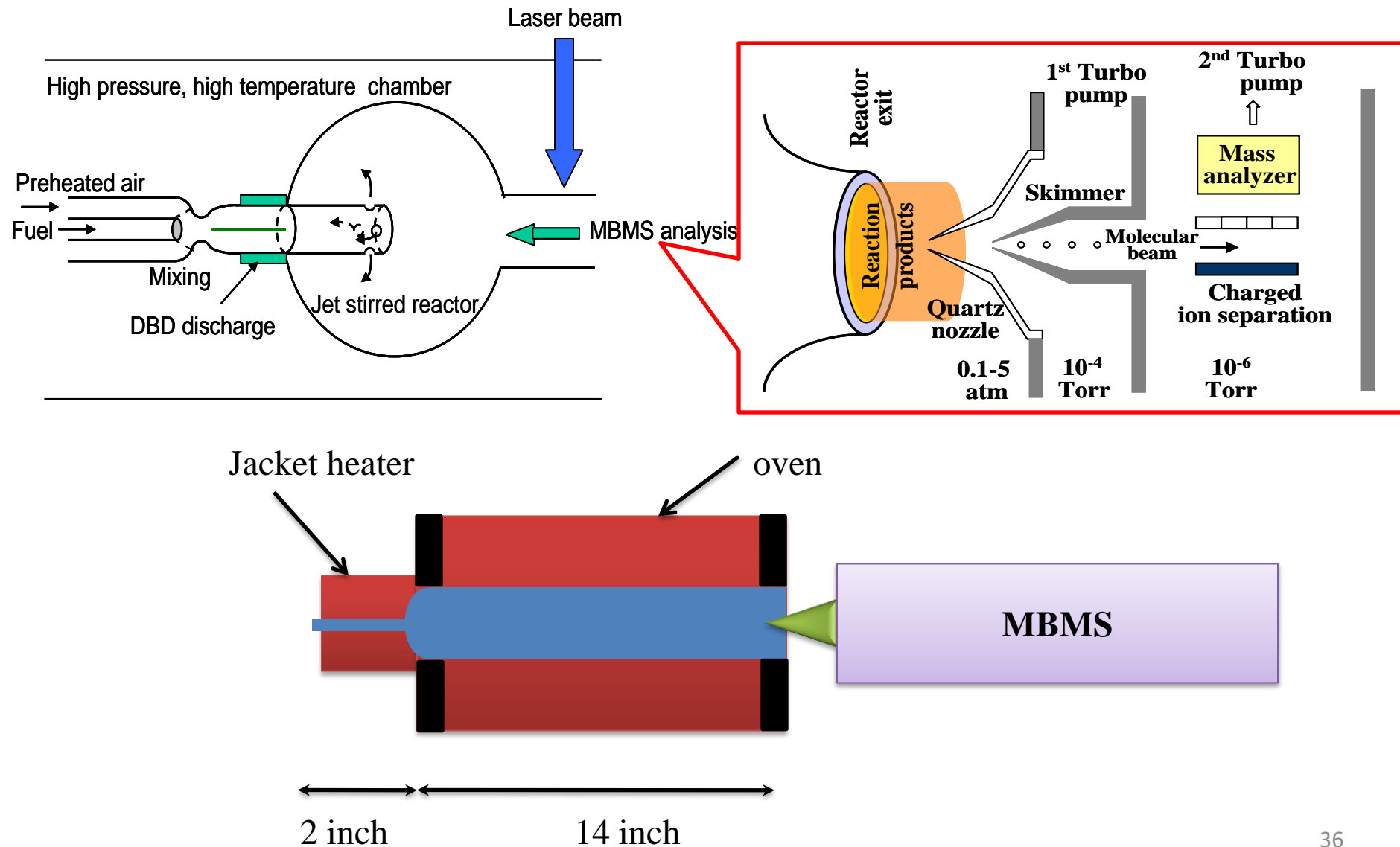
$\sigma$  : cross sections

$\chi$  : mole fractions





# Schematic of experiments with MBMS



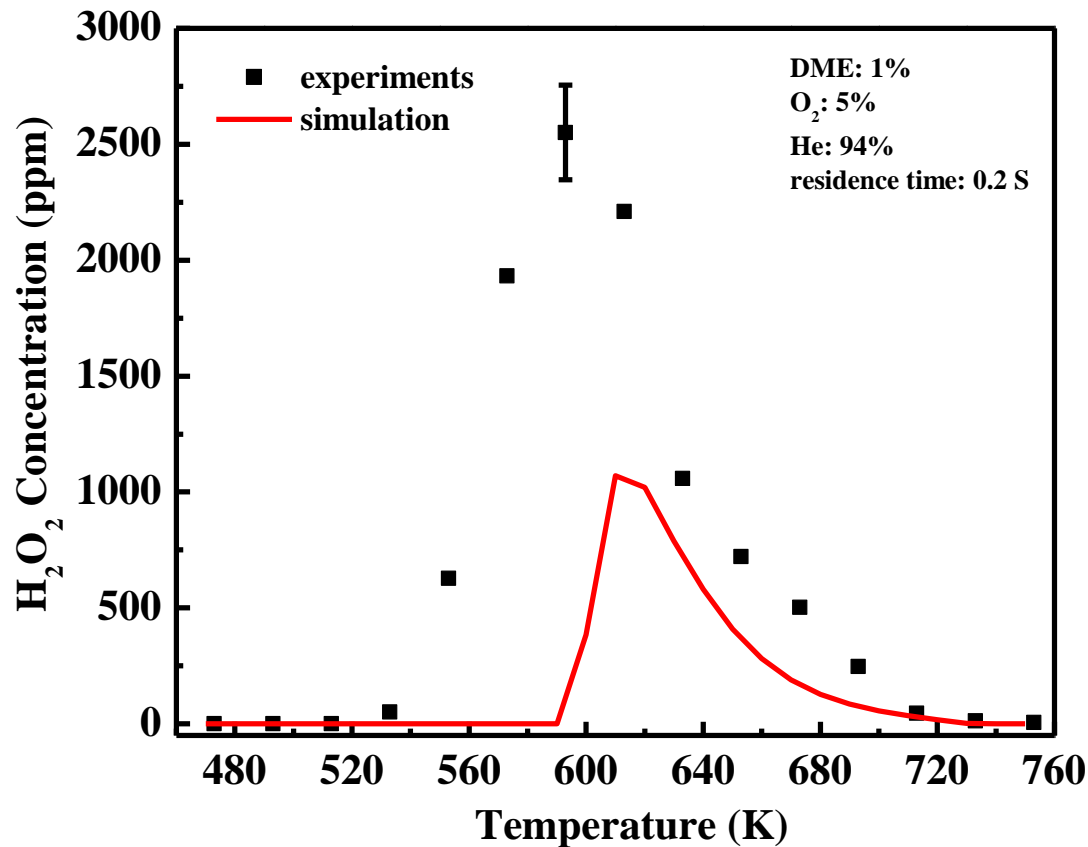


# Flow tube experiments

DME: rich low temperature chemistry

Pressure: 1 atm

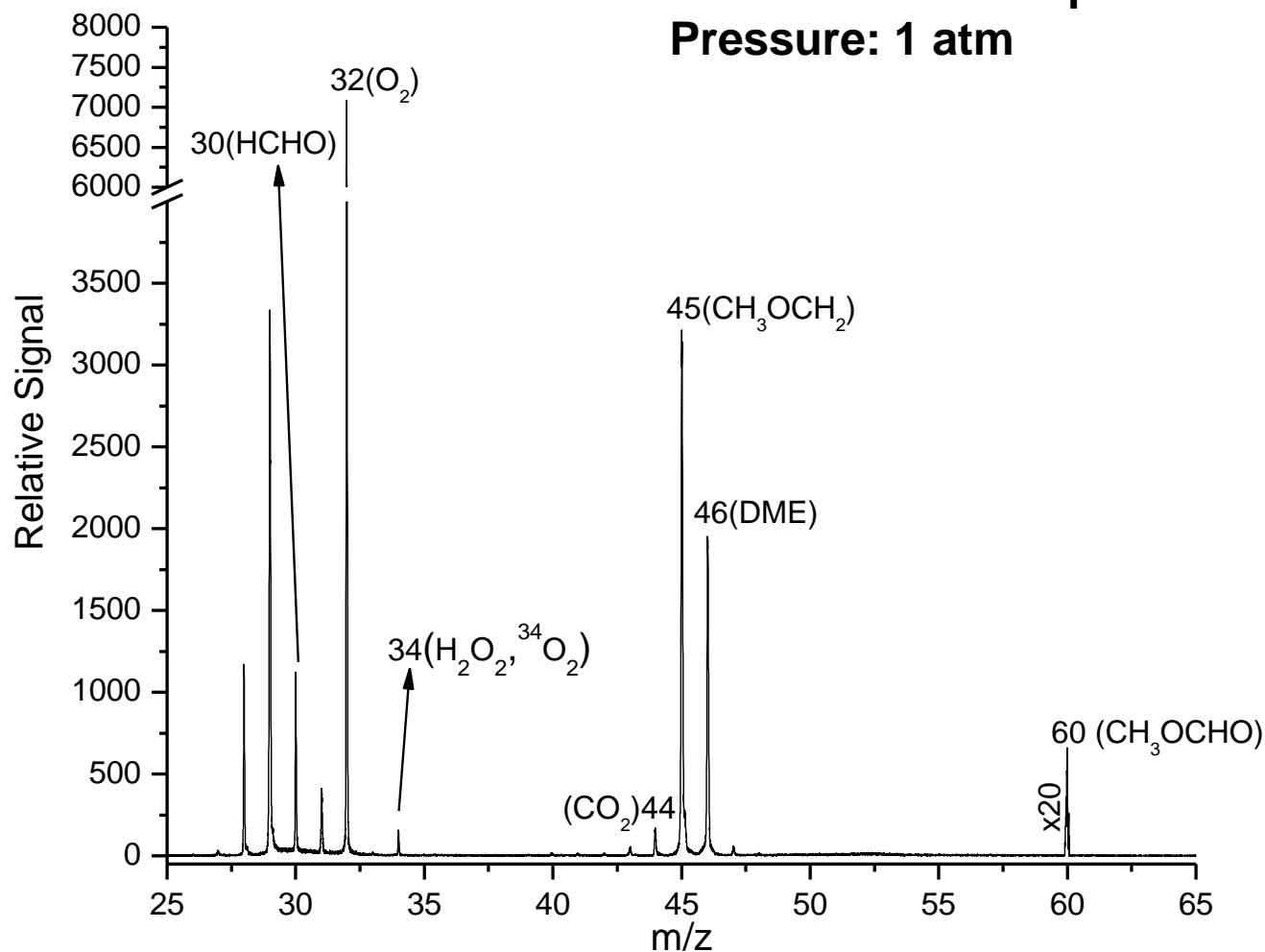
## $\text{H}_2\text{O}_2$ measurement





# Flow tube experiments

**DME: rich low temperature chemistry**  
**Pressure: 1 atm**





# Conclusions

1. Plasma can significantly accelerate the fuel oxidization at low temperature to extend the extinction limit dramatically.
2. Major kinetic pathways in plasma assisted combustion were identified .
3. A new counterflow burner with *in situ* discharge was developed. This burner provides a new platform to study kinetic effect of plasma assisted combustion.
4. The *In situ* discharge can maximize E/N at high T flame region, therefore, maximize the electron energy and effect on reaction zone, and enhance ignition and extinction.
5. The *In situ* discharge can dramatically enhance the ignition and modify the classical S-curve to be a monotonic curve.
6. MBMS was developed and  $\text{H}_2\text{O}_2$  was successfully measured directly for the first time in reacting system, enabling diagnostics of intermediate species in plasma assisted combustion at low T.





# Future work

## Plasma part:

1. OH PLIF for counter flow diffusion flame with *in situ* discharge and compare with simulations
2. Low temperature plasma assisted combustion for large alkanes
3. Flow reactor experiments on liquid fuel with QCL diagnostics on  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  and  $\text{HO}_2$
4. Develop validated plasma flame models

## MBMS part:

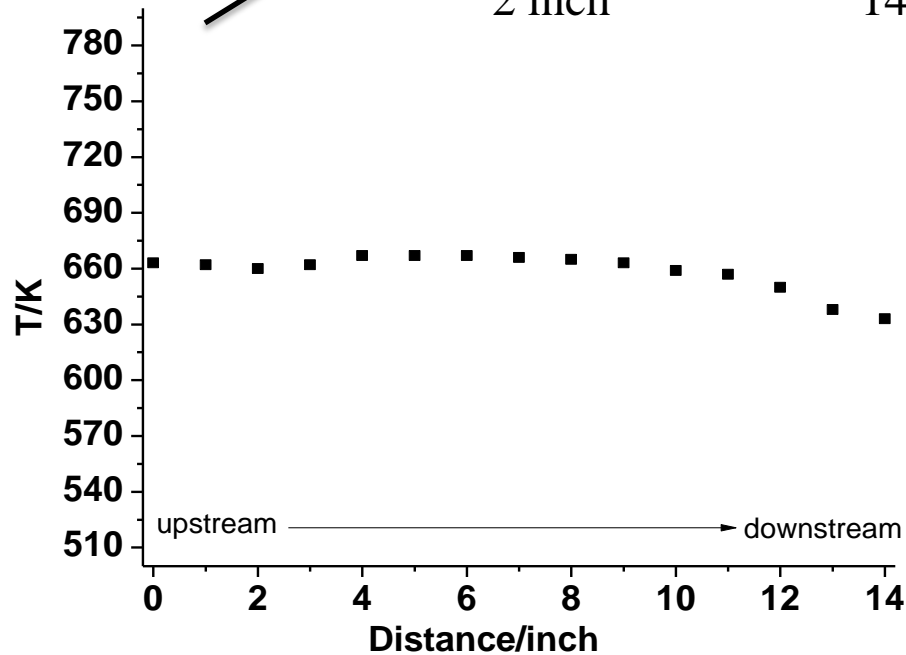
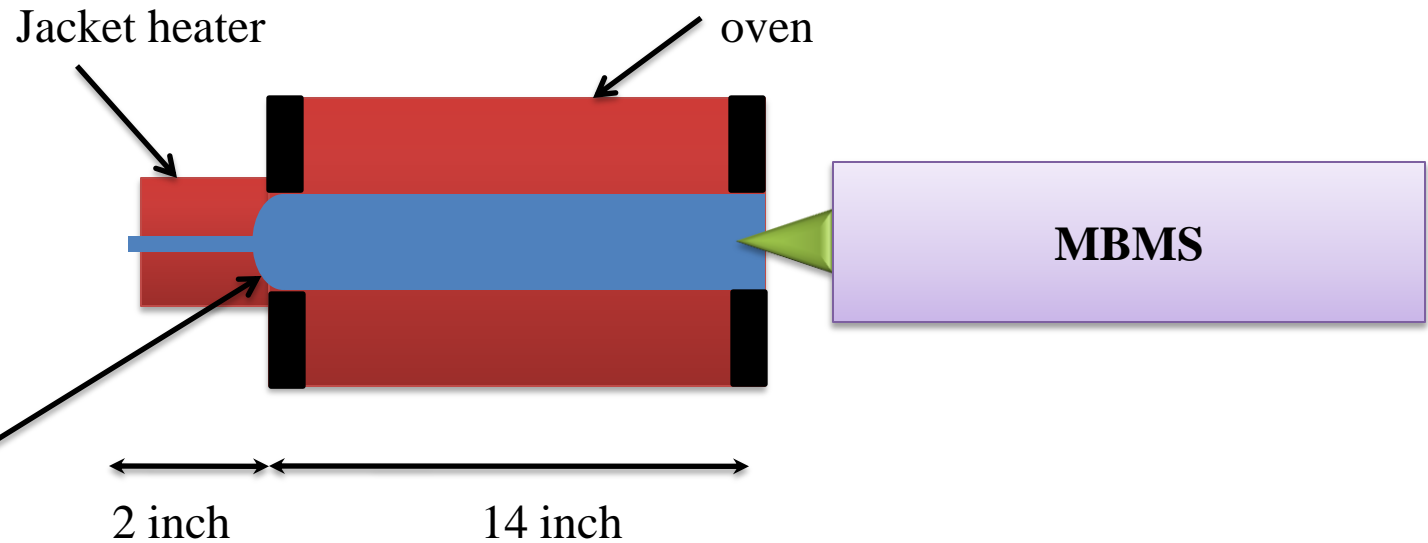
1. Develop a JSR to study the low temperature and high pressure chemistry
2. Integrate JSR with plasma discharge to investigate plasma chemistry
3. Develop advanced light source to ionize the molecular beam

**Thanks the support from AFOSR!**

**Questions?**



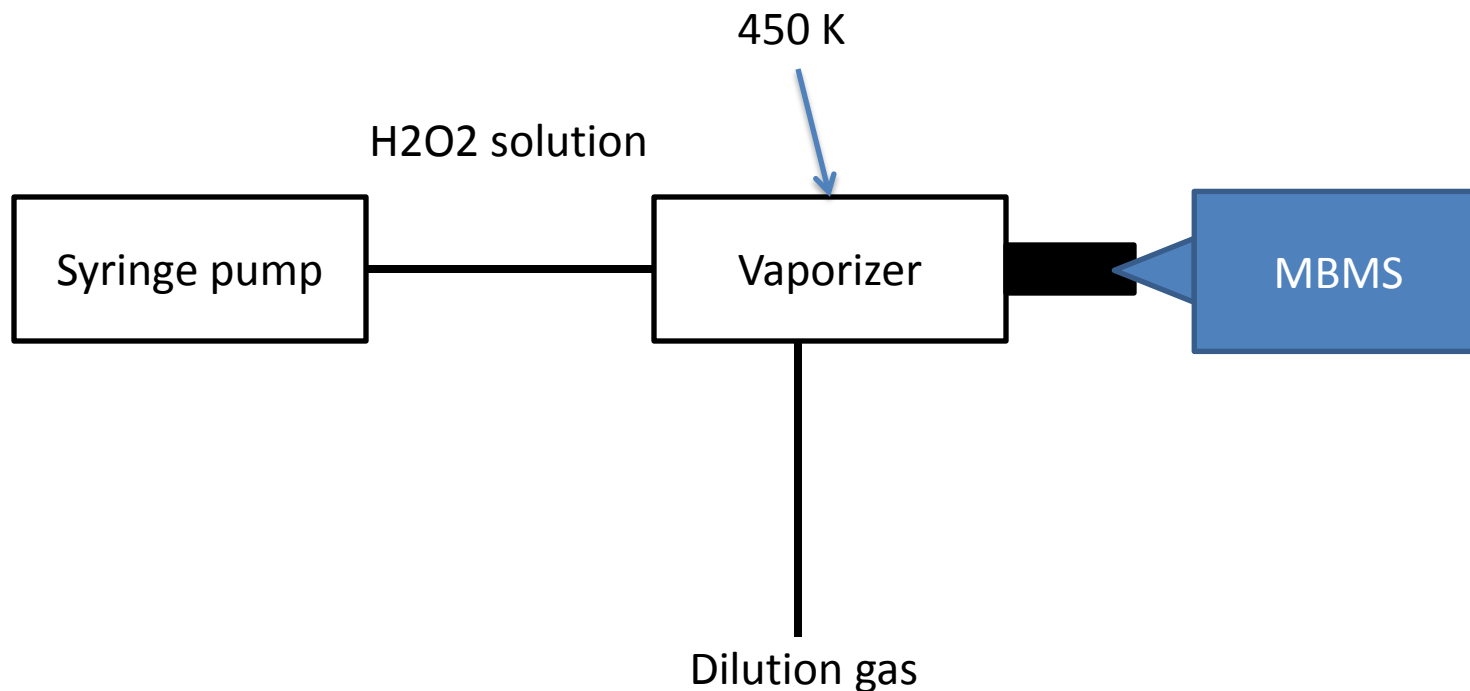
# Flow tube experiments

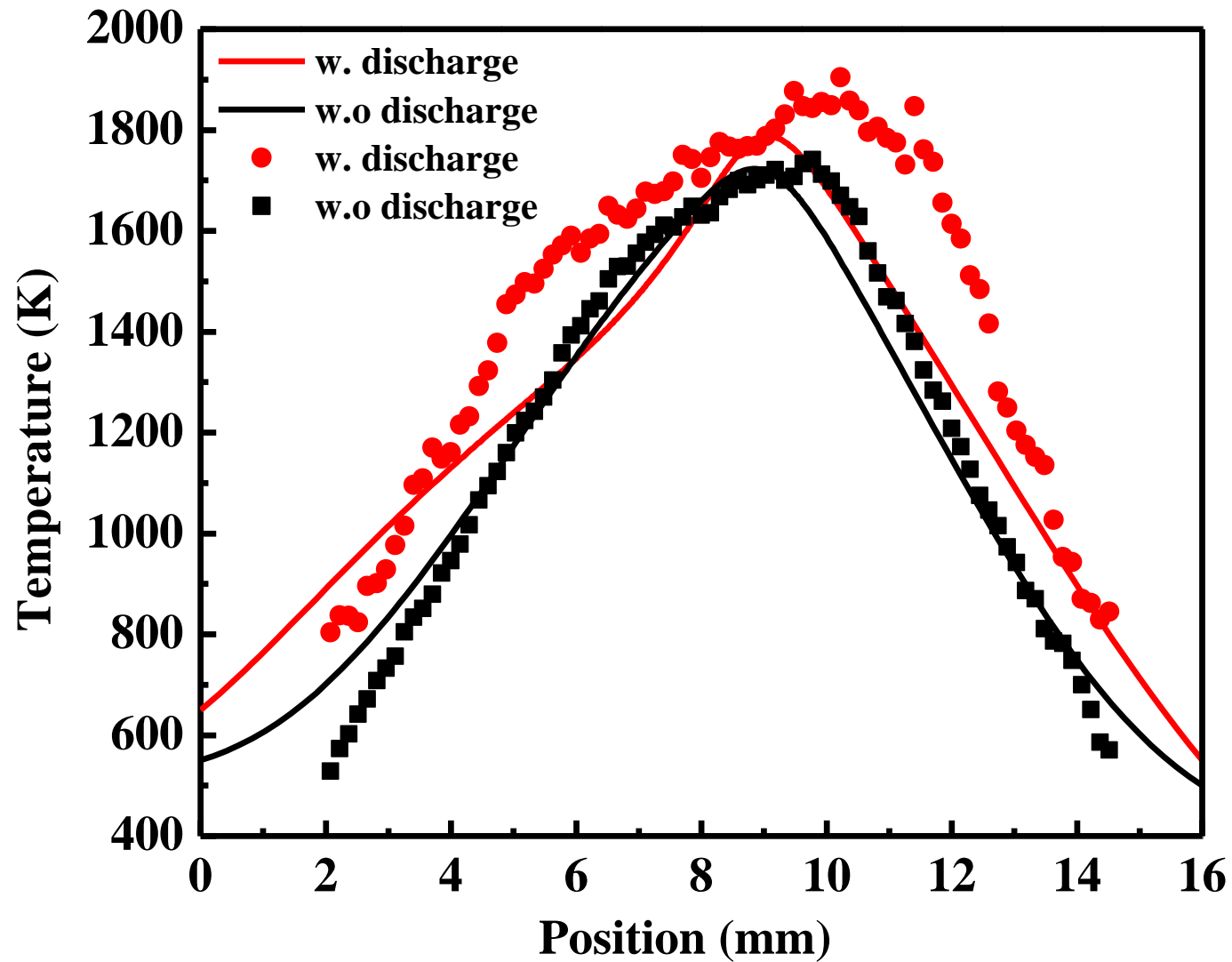




# H<sub>2</sub>O<sub>2</sub> calibration

Dissociation:  
do it quickly  
changing H<sub>2</sub>O<sub>2</sub> concentrations  
monitor O<sub>2</sub> peak





$\chi_{\text{O}_2} = 53.5\%$ ,  $\chi_{\text{CH}_4} = 20\%$ ,  $a = 400 \text{ 1/s}$